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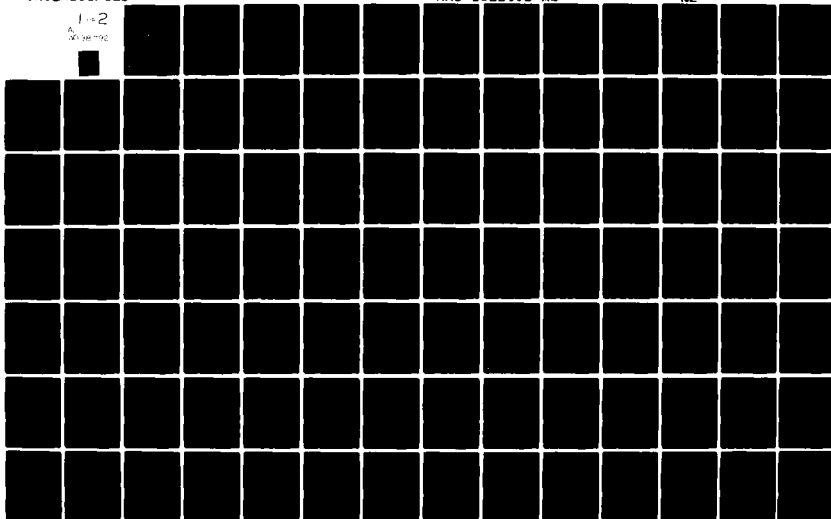
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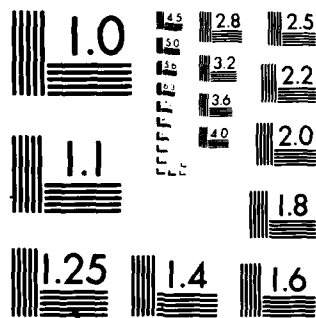
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- IV. Chemorheology.

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ABSTRACT

BUTADIENE-ISOPRENE BLOCK COPOLYMERS AND THEIR HYDROGENATED DERIVATIVES

In homopolymerization initiated by sec-butyl-lithium in hexane, isoprene is a more active monomer than butadiene (with $k_1 = 5.53 \times 10^{-5} \text{ sec}^{-1}$ vs. $k_1 = 0.98 \times 10^{-5} \text{ sec}^{-1}$ at 20°C). This is also true for reactions at 30° and 40°C . The apparent activation energy for both monomers has been found to be roughly the same, i.e., 19.4 kcal/mole. In the case of copolymerization, butadiene reacts preferentially, but nonexclusively. Significant amounts of isoprene units are also incorporated in a rather random fashion during the early stage of copolymerization. At 50 mole percent isoprene or higher, one observes a second stage of the polymerization that is faster and essentially identical to that observed for isoprene homopolymerization under similar conditions. Various methods have been used to estimate reactivity ratios. The average values at 20°C are $r_B = 2.64$ and $r_I = 0.40$. Preliminary evidence suggests that the copolymerization becomes more selective at lower temperature where the inversion phenomenon is more significant.

Star-branched homopolymers of butadiene and isoprene have been synthesized utilizing anionic polymerization techniques. The commercial mixture of divinylbenzene was employed as the star linking agent for the "living" polydiényllithium anions. The nature of the star-branching reaction was studied with respect to: the molar ratio of divinylbenzene (DVB/Alkylolithium (RLi), reaction temperature, reaction time and the nature of the polydiényllithium chain end. In general, a higher number of arms is achieved via increased DVB/RLi ratio, reaction temperature and through the choice of polybutadienyl chain ends. The polymers were characterized by gel permeation chromatography (GPC), membrane osmometry, intrinsic viscosity, and H-NMR spectroscopy. A Chromatix low-angle light scattering GPC detector was also employed for the determination of the weight average molecular weight (M_w), as well as a sensitive detector, which could assay absolute M_w versus elution volume profiles for a series of star-branched polyisoprenes and polybutadienes. The results indicate that under optimum conditions a relatively well defined number of arms can be achieved with DVB linking.

The effects of variation in molecular architecture and composition on bulk properties are reported for a series of well characterized hydrogenated block copolymers of butadiene (HB) and isoprene (HI) each having a total molecular weight of $\sim 200,000$ and a narrow distribution ($M_w/M_n < 1.17$). The polymers were synthesized from sequential anionic polymerization followed by hydrogenation, using p-toluenesulfonylhydrazide. The material properties of the homopolymeric HI and HB were also investigated. As expected, HI is rubbery at room temperature and HB is a tough semicrystalline plastic with properties similar to those of a low density polyethylene, LDPE. The crystallinity, density and ΔH_f for all of the block copolymers were found to be linearly dependent on HB content indicating that little mixing exists between the semicrystalline regions and the rubbery blocks. Although the solution cast films of the block copolymers were spherulitic, the quenched films displayed no distinct structure on the supermolecular level indicating that the aggregation of

the crystallites was more random in these films. The stress-strain properties of triblock copolymers with different block sequences, HBIB and HIBI, and a diblock copolymer, HBI, were similar in bulk behavior to each other in the high and the intermediate butadiene content (50-90%). This was related to the fact that the mechanical properties were determined predominantly by the behavior of the more continuous HB phase. For the lower butadiene compositions (7-29%), there was a major difference in the behavior of polymers with different block architecture. HBIB polymers were thermoplastic elastomers, whereas HIBI polymers behaved like an uncured particulate filled rubber. This difference was related to the presence of permanent "entanglements" in HBIB polymers. The permanent entanglements which act as a physical crosslink are a consequence of the anchorage of the HB end blocks in the semicrystalline domains. No such arrangement is possible for either the HIBI or HBI polymers. The hysteresis behavior of HBIB polymers were strongly dependent on butadiene content, decreasing with lowering of the concentration of the semicrystalline HB. This dependence was related to the continuity of the crystalline microdomains. All the members of HIBI (and the HBI we considered) showed large hysteresis behavior. This large energy loss during cyclic deformation in these polymers was related to the absence of the permanent anchor points arising from end block crystallization.

This work also emphasizes the novel chemorheological behavior of the isoprene-butadiene copolymers. This behavior was studied by both continuous and intermittent stress-relaxation of dicumyl peroxide crosslinked gum vulcanizates. The degree of crosslinking was maintained at approximately the same level ($M_c = 5,300$) at all compositions and was assessed by both swelling and equilibrium stress-strain moduli. At relatively high temperatures, there are two competing processes that affect the mechanical property of the copolymers. The first may involve both reversible chain scission and rapid crosslinking while the other is irreversible chain scission. The first of these most important degradative reactions is dominant in poly(butadiene) while the second seems to be in poly(isoprene). However, in the block copolymers studied, the behavior of the samples was dependent on the composition but was independent of the molecular architecture. The systematic behavior displayed by the polymers suggest a well-mixed morphology, as has been reported by others, using more conventional methods for miscibility assessment.

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I. Anionic Copolymerization of Butadiene and Isoprene with
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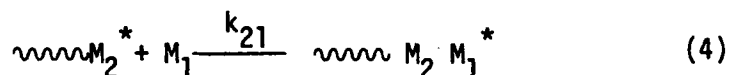
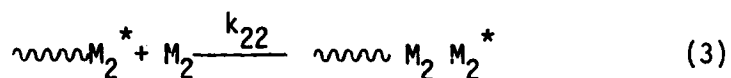
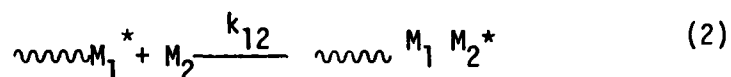
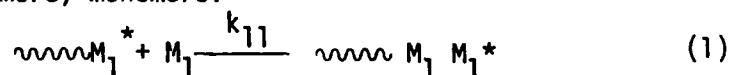
ANIONIC COPOLYMERIZATION OF BUTADIENE AND ISOPRENE
WITH ORGANOLITHIUM INITIATIONS IN HEXANE

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INTRODUCTION

Copolymerization, of course, involves the simultaneous polymerization of a mixture of two (or more) monomers.



In its most simplified form, one assumes a steady state and thus deals with the probabilities of an activated macromolecular chain end either adding another chemically identical unit, eq. its own monomer, or "cross-initiating" the second monomer. The latter situation amounts to a copolymerization and is illustrated schematically in equations (2) and (4) above. Typically one defines reactivity ratios r_1 and r_2 on the basis that:

$$r_1 = \frac{k_{11}}{k_{12}} \quad \text{and} \quad r_2 = \frac{k_{22}}{k_{21}}$$

The most studied activated chain ends are the macromolecular free radicals. Vast numbers of monomers have been investigated ⁽¹⁾ in hopes of identifying new random (statistical) copolymers which might show a favorable balance of averaged physical properties. In the case of free radical intermediates, one must be very much concerned with both the radical lifetime and the need for a facile cross-initiation. Otherwise, premature termination can lead to generation of (usually) incompatible homopolymers which in turn possess rather unattractive physical properties. ⁽²⁾ In the case of anionic copolymerization, the "living end" must still make a choice between reacting with its own monomer or the second monomer. Relative basicities are an important consideration. ^(3,4) However, for organolithium initiated polymerizations of butadiene, isoprene or styrene in hexane, cyclohexane or benzene, it is possible to study homogeneous termination free systems. The reactivity of the carbanion end would be expected to be dependent on several parameters such as the counterion, solvent, temperature, etc. It is known for example, that carbanions can exist in "tight", "loose", or even "free" structures as a function of counterion and solvent. ^(5,6) In hydrocarbons, one should expect organolithiums to exist in more or less tight ion-pairs. Perhaps the most investigated anionic system is the organolithium initiated copolymerization of the monomer pairs, styrene-butadiene and styrene-isoprene. ⁽⁷⁾ In hydrocarbon solvents, it is the diene which dominated the initial copolymerization to the virtual exclusion of styrene, and one observes a rate nearly identical to that of the diene alone. ^(9,10) Only when the diene supply is nearly depleted does styrene begin to be incorporated in the polymer chain. Interestingly, a faster polymerization rate is then observed for the styrene segment. Thus in these systems, there is an apparent "reversal of reactivity" of styrene and the diene, since for the homopolymerization situation, styrene is a much more reactive monomer than either diene.

Relatively little information is available for the copolymerization of butadiene with isoprene. In an early paper by Rakova and Korotkov⁽⁸⁾, it was concluded that in n-hexane with n-butyllithium as the initiator, the reactivity ratios for butadiene and isoprene were $r_B=3.38$ and $r_I=0.47$, respectively. In other words, the butadiene monomer reactivity significantly differs from isoprene but by a smaller factor than for a styrene-diene system. Nevertheless, the phenomenon of "reversal of reactivity" still reportedly occurred in the copolymerization between these two dienes. We felt that if these values were essentially correct that relatively pure blocks of butadiene might well be formed at the early stage of reaction by directly copolymerizing butadiene and isoprene simultaneously. We are quite interested in synthesizing block-type thermoplastic elastomers of this type. The butadiene-isoprene-butadiene copolymer per se may not be influenced by architecture arrangement. However, in the totally or selectively hydrogenated derivatives, one might expect major differences if there are crystallizable polyethylene blocks derived from the 1,4 butadiene units in polyethylene-poly(ethylene-co-propylene) or polyethylene-polyisoprene block copolymer. By analogy with the styrene-diene⁽⁷⁾ systems, the crystalline polyethylene end blocks in the triblock should associate to form crystalline tie-down points which will desirably reinforce the soft interior block of polyethylene-co-propylene or polyisoprene in the resulting two hydrogenated copolymers. Our kinetic investigation was thus principally motivated by the desire to learn whether the possible "reversal of reactivity" between butadiene and isoprene via anionic copolymerization would be of sufficient magnitude to produce crystallization sequences in the hydrogenated derivatives. We were also interested in investigating possible subtle temperature or solvent effects. High vacuum techniques were employed⁽¹²⁾ with the view that this work might improve

on the research published two decades ago.⁽⁸⁾ Our new results on the reactivity ratios for butadiene and isoprene have also been analysed via both conventional^(13,14) and the more recent statistical methods.⁽¹⁵⁻¹⁸⁾

EXPERIMENTAL

Copolymerization Apparatus and Techniques

The high reactivity of alkyl lithium compounds requires that these polymerizations be performed under extremely high purity conditions. In order to achieve this we have utilized a high vacuum system. The basic design of a high vacuum apparatus and purification procedures have been described in detail elsewhere.⁽¹²⁾ Accordingly, the required techniques used for the purification of n-hexane, the monomers and the sec-butyllithium initiator have thus been performed. A typical glassware reactor which also permits purging of the reaction vessels is shown in Figure 1. The reactors were always flamed at a constant pressure of 10^{-5} mm Hg until the flame took on the characteristic sodium color. It was then sealed off the vacuum system, purged with n-butyllithium/hexane solution and rinsed with hexane by back distillation at least four times. The purging section was then sealed off the reactor. Initiator which has previously been vacuum distilled and diluted with pure hexane was used. A measured volume and known concentration was introduced from the attached ampoule into the reactor, followed by careful rinsing again with hexane. The purged reactor was then sealed onto the vacuum line through one of the break seals. The additional solvent and monomers were then quantitatively distilled in. Volumes were recorded at suitable low temperatures (e.g. -78°C) where density values were available. The values of 0.73 gm/cc for butadiene at -78°C and 0.68 gm/cc for isoprene at 20°C were used. It should be stressed that the sealing of all constrictions or dilatometers was performed with the solution frozen or cooled down at -196°C or -78°C , respectively.

Kinetic Study

Four to six dilatometers (2 mm inner bore) of 3-5 ml each were attached to one of the side arms of the reactor shown in Figure 1. The actual solution volume depended on the monomer concentration and was usually adjusted to allow about a 10-15 cm drop at 100% conversions. After the contents of the reaction were equilibrated near room temperature, the dilatometer volume was usually adjusted such that the stems were about half-full. To prevent any undesirable distillation and/or bumping which would cause concentration fluctuations, the procedures outlined by Juliano⁽¹⁹⁾ were carefully followed. Next, each detached dilatometer was securely clamped in a constant temperature bath which was maintained at 20, 30, or 40°C as desired. Readings were taken with a cathetometer after the initial thermal expansion to the bath temperature. The data were treated as described by Pett.⁽²⁰⁾ The dilatometric treatment was also used for those reactions where a conversion versus time curve was required for later estimation of extent of conversion.

The extent of conversion was cross-checked by precipitation of the polymer into methanol, followed by filtration and drying at room temperature under mechanic pump vacuum ($\sim 10^{-2}$ Torr) until constant weight was attained.

The composition of the copolymer was determined by either NMR analysis at 90 MHz according to the equations derived by Mochel⁽²¹⁾ or by infrared.⁽²²⁾ The agreement of these methods was $\pm 2\%$ when applied to copolymer taken to 100% conversion. The reactivity ratios were calculated according to the Mayo-Lewis Plot^(13,15) the Fineman-Ross Method⁽¹⁴⁾, or by the Kelen-Tudos equation⁽¹⁶⁻¹⁸⁾. The statistical variations recently noted by O'Driscoll⁽²³⁾, were also considered.

The total hydrogenation of the copolymers utilized the diimide method⁽²⁴⁾, generated in the situ from p-toluenesulfonylhydrazide (TSH) in xylene for six

hours at reflux temperature (132-134°C). In general, 5.0 moles of TSH per 100 grams of polymer were used. We have found⁽²⁵⁾ that the addition of a phenolic antioxidant such as Irganox 1010 effectively decreases the minor, but detectable side reactions. The saturation of the polydiene was determined to be complete either by high temperature H-NMR analysis in hexachloro-1,4-butadiene using hexamethydisiloxane as an internal standard, or by infrared spectra of the polymer film cast on a KBr plate. Thickness of between 1/2 to 1 mil was required for a good spectra. The hydrogenated copolymers were further checked for crystallinity content on a Model 2 Perkin-Elmer differential scanning calorimeter (DSC) at a heating rate of 20°C/minute.

RESULTS AND DISCUSSION

Homopolymerization of Butadiene and Isoprene in n-Hexane

Homopolymerizations were first conducted to establish a basis for the copolymerization study. The polymerization of the diene monomers in n-hexane has been investigated in the literature via two approaches: (a) by mixing all of the monomers and solvent directly with initiator, and (b) by premixing all of the initiator with a slight molar excess of the monomer, to form a living "seeded" polymer. The later method was particularly employed with n-butyllithium initiators⁽²⁶⁾ where the initiation rate was slow enough that the sample organolithium persisted during a substantial period of the polymerization process. In order to enhance the rate of initiation relative to that of propagation, sec-butyllithium has evolved⁽²⁷⁾ as the preferred initiator, especially for kinetic studies. Branched alkylolithiums have been reported to increase the initiation rate of dienes in hydrocarbon solvents.⁽²⁸⁾ When the initiation rate is of the same order of magnitude as the rate of propagation, the homogeneous anionic polymerizations allows the synthesis of polymers possessing a very narrow molecular weight distribution. Relatively

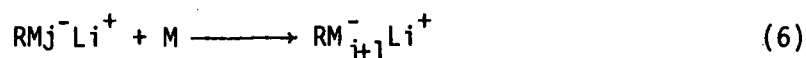
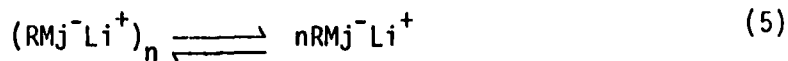
linear polymerization curves can be obtained for both butadiene and isoprene as shown for example in Figure 2. This was true at three different temperatures, namely, 20°, 30°, and 40°C.

The kinetic results obtained by dilatometry for the polymerization of butadiene and isoprene are shown in Figures 3 and 4. As usual, ΔH_t refers to the change in height at a given time. It can be seen that the kinetic studies on dienes confirm that the propagation reaction has a first-order dependence on the monomer concentration. These observations are to be expected since in this absence of adventitious impurities the number of growing chains should remain constant, only the monomer concentration decreases.

The observed apparent first-order rate constants are listed in Table I. From the constants at different temperatures but at the same initiator concentration, it is possible to calculate an apparent activation energy for the propagation reaction in each case. This has been done, and the Arrhenius plot is shown in Figure 5. It is interesting to note the similarity of these activation energies, $19.2 \text{ kcal/mol}^{-1}$, for polymerization of the two monomers in n-hexane. The values obtained are much higher than what has been reported for the case where THF is the solvent.⁽²⁶⁾ Our value is also somewhat higher than the 14.3 k-cal/mole published by Worsfold and Bywater.⁽²⁹⁾ From the viscosity studies of Morton, et. al.,^(30,31) one may assume that the active poly(dienyl)-lithium is associated in pairs in n-hexane, but no such association is observed in THF. On this basis, the high activation energy found for the propagation reactions in n-hexane also includes the heat of dissociation of the associated ion pairs.

The dependence of the propagation rate on the concentration of growing chains is illustrated in Figures 6 and 7, and is listed in Table II. The first-order rate constant from Table II are plotted as a function of the initiator concentration. Although the kinetics of organolithium polymerization in nonpolar

solvents have been subjected to intensive study. The results are still somewhat controversial. In view of the strong experimental evidence for association between the organolithium species, the kinetic order ascribed to this phenomenon was postulated^(30,31) as shown in equations (5) and (6).



This assumes that only the dissociated chain ends are active. Actually, measurement on the state of association, i.e., the value of n in equation (5), have been carried out for styrene, butadiene and isoprene, and have been found to be consistently very close to 2. While this could explain the half-order kinetics found by most investigators⁽¹²⁾ in the case of styrene, it cannot account for the lower orders (1/4 to 1/6) found for butadiene and isoprene in various hydrocarbon solvents. Our data are plotted, in Figure 6, as a function of initiator concentrations and apparently fit a 1/4-order type kinetics, especially for the case for butadiene at 20°C. The same kinetics data for isoprene at 30°C shown in Figure 7, are not as precise but are plotted on the basis of a 1/4-order dependence. However, our results confirm the idea that the propagation rates of the diene monomer in hydrocarbon are certainly a fractional order type dependence. Whether 1/4-order or something different order probably needs to be further defined. Nevertheless, it appears that the propagation reaction of these associated growing chains in nonpolar media may be more complicated than proposed in equations (5) and (6), and probably involves a direct interaction between the monomer and the associated complex.⁽³²⁾

Kinetic Study on the Copolymerization of Butadiene and Isoprene in Hexane

It has been emphasized in the copolymerization of styrene with butadiene or isoprene in hydrocarbon media, that the diene is preferentially incorporated.^(7,9,10)

The rate of copolymerization is initially slow, being comparable to the homopolymerization of the diene. After the diene is consumed, the rate increases to that of the homopolymerization of styrene. Analogously our current investigation of the copolymerization of butadiene with isoprene shows similar behavior. However, the reversal of reactivity is much less. The degree of reversal phenomenon among these two dienes can be correlated with the reaction temperature for a fixed monomer feed ratio. The dilatometric data are plotted in Figures 8-10 for three different temperatures, and are summarized in Table III for the purposes of clarity and comparison. Curves 1 and 5 in these figures represent the homopolymerization rates of isoprene and butadiene, respectively. In addition, data for three different initial monomer feed ratios are expressed by B/I's with 25/75, 50/50, and 75/25. The numbers denote the monomer ratio of butadiene content to isoprene for curve 2, 3, and 4, respectively. The initial propagation rate constants were measured and are listed in Table III, along with the homopolymerization rates of butadiene and isoprene under the same conditions. For higher contents of butadiene (i.e. with a mole fraction of 0.75), the overall copolymerization rate is almost identical to the homopolymerization rate of butadiene. This behavior was observed at three different temperatures, 20°, 30°, and 40°C. Curve 4 shown in Figures 8-10 is almost parallel to Curve 5, and shows no sign of the inversion phenomenon. Accordingly, during the copolymerization with a butadiene-to-isoprene molar ratio of 75 to 25, there is a considerable amount of isoprene incorporated in a rather random fashion with the butadiene. The overall rate is nevertheless controlled by the slower rate-determining step of butadiene polymerization. The copolymer composition at low conversion has been determined to be rich in butadiene, for example 83.5 to 88.5 mole% were found compared to 75 mole% in charge (cf also Table IV). However, when a mixture of butadiene and isoprene with 25/75 or 50/50 molar ratio is polymerized, the initial propagating rate is enhanced slightly due

to the isoprene. All the prematurely terminated copolymers with butadiene mole fraction from 0.20 to 0.80 in the feed are nevertheless found to be rich in butadiene, as seen by the copolymerization data listed in Table IV. Moreover, there is another interesting point observed with the molar ratios of butadiene to isoprene of 25/75 or 50/50. Here one can observe the occurrence of the "inversion" phenomenon which is manifested by the inflection point of the kinetic curve 2 and 3 of Figures 8-10 at all three temperatures. The lower the copolymerization temperature, for example 20°C, the sharper the inflection appears to become. This behavior leads to the conclusion that the copolymerization is more selective at lower temperatures. Conversely, when temperature is increased selectivity is noticeably decreased. The derived reactivity ratios reflect this trend and are shown in Table V.

By measuring the kinetic rate of second stage reaction after inflection, one can observe that rate is very analogous to the homopolymerization rate of isoprene. The data are listed in Table III, and can also be detected by the straight portion of Curves 2 and 3 after inflection. The "inversion" phenomenon can be easily explained by the fact that, although the isoprene is more reactive than butadiene in homopolymerization, in a mixture butadiene tends to preferentially (not exclusively) polymerize first with some random incorporation of isoprene units. After the butadiene is depleted at first stage of copolymerization, the isoprene rate does eventually take over.

One can try to explain the reversal of reactivity of butadiene and isoprene during copolymerization in hexane solvent. A number of different effects may be important. Major parameters include the electronic and steric character of the monomers and how they may relate to the slow step of the polymerization. One might argue that the electron-donating methyl group on isoprene could decrease the electrophilic character of isoprene and render it less reactive toward a

living carbanion end. However, one must also recall that the homopolymerization rate is higher! The copolymerization of butadiene, isoprene, and 2,3-dimethylbutadiene with polystyryl sodium in tetrahydrofuran solution showed a retarding effect of the methyl group on the addition of diene.⁽³³⁾ Again, though these results were in THF, not hexane, where association effects are important. Steric effects possibly related to the 4,1 nature of the active chain, seems to be a more likely possibility.

The NMR analysis⁽²¹⁾ of the chemical composition for copolymers from various monomer feed ratios at fairly low conversion are shown in Table IV. The results were then used to estimate the reactivity ratios for the diene monomers. Various published methods of calculating monomer reactivity ratios have been examined. These include the once popular but now somewhat out of favor Fineman-Ross method⁽¹⁴⁾, the graphical Mayo-Lewis Solution⁽¹³⁾ modified by Joshi-Joshi estimation⁽¹⁵⁾, and the recent Kelen-Tüdös method.⁽¹⁶⁻¹⁸⁾ The results are all summarized in Table V. Although the determination of reactivity ratios based on the usual relation between copolymer composition and monomer ratio can only be considered as an approximation, the values recorded in Table V do indicate a trend, that the ratios differ by a slightly greater factor at 20°C than at 30°C or 40°C. This observation is corroborated with what has been found in Figures 8-10. There is more of an inversion phenomenon occurrence at 20°C. However, the difference between 30°C and 40°C is small and apparently similar, within experimental error. Nevertheless, the new established reactivity ratios of butadiene and isoprene at all three temperatures differ by a smaller factor than what were reported by the work of Korotkov⁽⁸⁾, (e.g. $r_1 = 3.38$ and $r_2 = 0.47$). Moreover, butadiene is more reactive and initial copolymer contains a larger proportion of butadiene randomly placed along with some incorporation of isoprene units. The randomness of the copolymer via direct copolymerization has been confirmed by the comparison with pure diblock copolymer

produced by sequential monomer addition. Both copolymers have similar chemical composition (50/50) and molecular weight. Their characterization data are presented in Table VI. The near "monodispersities" were also confirmed by the GPC measurements. After hydrogenation via diimide in situ the block copolymer of polybutadiene-polyisoprene produces a polyethylene-poly(ethylene-co-propylene) system. The partially crystalline blocks of "polyethylene" show melting point about 100°C by DSC as shown in Figure 11. Parallel behavior has also been reported for partially hydrogenated polybutadiene in the literature.⁽³⁴⁾ The properties of our hydrogenated polymers are interesting and are reported elsewhere.⁽³⁵⁾ For the copolymer made via direct copolymerization with butadiene-to-isoprene weight ratio of 50 to 50, its totally hydrogenated derivative shows different pattern. Only a very small melting transition at 92°C can be seen in the DSC thermogram. This indicated that only an insignificant portion of polyethylene has been induced through hydrogenating the copolymer block rich in polybutadiene. The sequence length of the polybutadiene is shortened by the incorporation of some isoprene. The isoprene units thus eliminate the crystallinity in the subsequently hydrogenated material.

CONCLUSIONS

In the current study of the homopolymerization and copolymerization of butadiene and isoprene by secondary-butyllithium in hexane the following conclusions can be made.

(1) Isoprene is a more active monomer than butadiene in homopolymerization, but the apparent activation energy of the propagation reaction is 19.2 kcal/mole for both monomers.

(2) In copolymerization butadiene reacts preferentially, however, significant concentration of isoprene units are also incorporated in a random manner during the early stage of reaction. Butadiene has higher reactivity ratio than

isoprene. The reversal of reactivity is caused by the less steric and polar factors in the interaction of butadiene molecules with an active anionic center.

(3) Interestingly, kinetic results show that essentially pure isoprene blocks are formed in the latter stage of reaction after "inversion" point. The phenomenon is somewhat dependent on the relative molar concentration and temperature.

(4) Various methods have been applied to estimate their reactivity ratios which are tabulated in Table V. Typical values at 20°C are $r_B = 2.64$ and $r_I = 0.404$. Preliminary evidence was reported that suggests the copolymerization is more selective at lower temperatures.

ACKNOWLEDGEMENT:

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Table I
First-Order Propagation Rate Constants (k_1) of the
Homopolymerizations of Butadiene and Isoprene

System	Temp. °C	[sec-BuLi] ₀ mole/l. x 10 ³	[Monomer] ₀ mole/l.	k_1 , sec ⁻¹ x 10 ⁴
Butadiene -Hexane	20	1.27	1.00	0.0978
	30	1.27	1.00	0.327
	40	1.27	1.00	0.796
Isoprene -Hexane	20	1.26	1.00	0.553
	30	1.26	1.00	1.48
	40	1.26	1.00	4.56

Table II
Effect of Initiator Concentration of the Propagation
Rate of Butadiene and Isoprene in Hexane

System	Temp. °C	[sec-BuLi] ₀ mole/l. x 10 ³	[Monomer] ₀ mole/l.	k ₁ , sec ⁻¹ x 10 ⁴
Butadiene -Hexane	20	0.683		0.0802
		1.27	1.00	0.0978
		2.54		0.121
Isoprene -Hexane	30	0.704		0.967
		1.26	1.00	1.482
		2.51		1.769

Table III

Summary of Kinetic Results for the Homo- and Co-Polymerizations of Butadiene and Isoprene in Hexane

Curve #	Monomer Feed Ratio B/I	Temp. °C	[sec-Buli] mole/l. $\times 10^3$	Propagation Rate Constant k_p (sec ⁻¹) $\times 10^4$	
				Initial	After inversion
1	0/100	20	1.26	0.553	
		30		1.48	
		40		4.56	
2	25/75	20	1.22	0.126	0.514
		30		0.450	1.324
		40		1.382	4.95
3	50/50	20	1.26	0.105	0.710
		30		0.359	1.244
		40		1.076	4.52
4	75/25	20	1.31	0.0979	no inversions
		30		0.320	
		40		0.864	
5	100/0	20	1.27	0.0978	
		30		0.327	
		40		0.796	

Table IV
Anionic Copolymerization Data

System	Feed Mole % Butadiene	Temp °C	Copolymer Composition mole % Butadiene	Conversion Wt %
Butadiene/Isoprene/Sec-BuLi/Hexane	20	20	37.3	2.63
		30	37.2	4.40
		40	38.9	10.37
	30	20	54.2	3.47
		30	46.8	6.08
		40	48.2	9.06
	40	20	62.3	5.52
		30	58.0	4.08
		40	61.7	7.56
	50	20	72.7	4.58
		30	66.3	5.10
		40	69.7	10.62
	60	20	80.0	2.66
		30	74.3	8.33
		40	77.7	14.75
	75	20	88.5	10.00
		30	83.5	38.00
		40	--	--
	80	20	91.3	4.94
		30	87.1	9.67
		40	88.1	11.82

Table V
Copolymerization Reactivity Ratios
of Butadiene (M_1) and Isoprene (M_2) initiated by Sec-BuLi in Hexane

Temperature °C	Reactivity Ratios			
	FR (a)	Inverted FR (b)	ML -JJ (c)	KT (d)
20	$r_1 = 2.62$	2.71	2.62 ± 0.06	2.64
	$r_2 = 0.39$	0.43	0.39 ± 0.07	0.40
30	$r_1 = 1.57$	1.60	1.68 ± 0.09	1.60
	$r_2 = 0.33$	0.35	0.36 ± 0.08	0.35
40	$r_1 = 1.74$	1.97	1.82 ± 0.071	1.89
	$r_2 = 0.24$	0.34	0.28 ± 0.09	0.32

(a) FR = Fineman-Ross Method

(b) Inverted FR = Inverted Fineman-Ross Method

(c) ML -JJ = Graphical Mayo-Lewis Method modified by Joshi-Joshi estimation

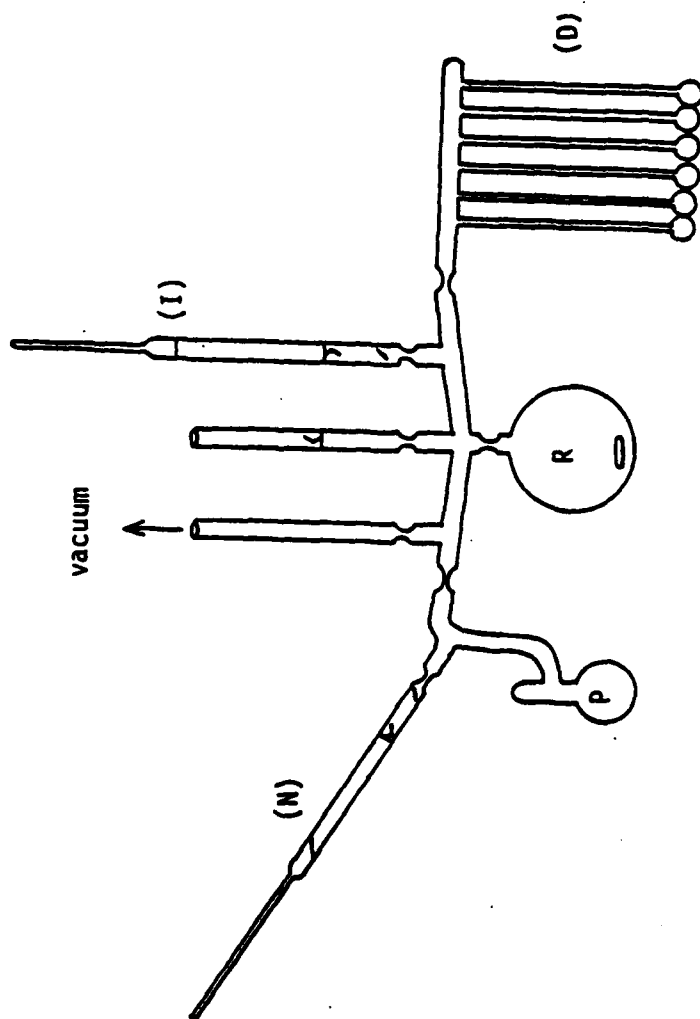
(d) KT = Kelen-Tüdös Method

Table VI
Comparison of Copolymers via Sequential and Direct Monomer Addition

Curve #	Total Hydrogenation of Polymer Code #	Monomers Addition	wt % PB/PI	M_n (a) ($\times 10^{-3}$)	M_w (b) ($\times 10^{-3}$)	$[\eta]$ 25°C THF
1	9-ICW-29	Sequential	49/51	190	208	1.80
2	9-ICW-88	Direct	48.8/51.2	183	213	2.24

(a) Determined via membrane osmometer in chlorobenzene at 25°C.

(b) Obtained from gel permeation chromatography calibration curve.



- (I) Initiator Ampoule
- (D) Dilatometers
- (R) Reactor
- (P) Purging Solution Collector
- (N) N-Butyl Lithium in Hexane Solution

Figure 1. Copolymerization Purging Apparatus and Reactor with Attached Dilatometers

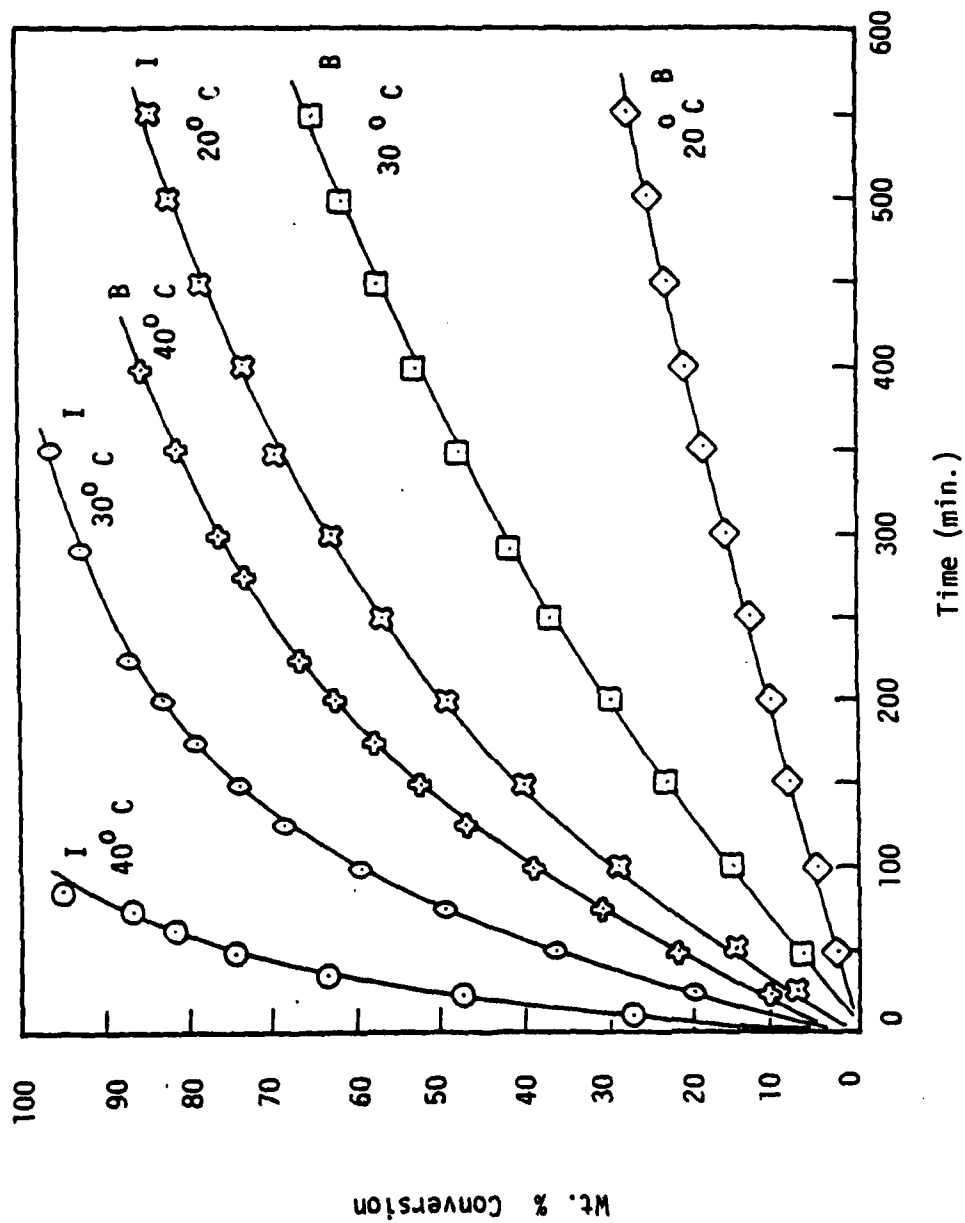


Figure 2. Homopolymerization Rates of Butadiene and Isoprene in Hexane

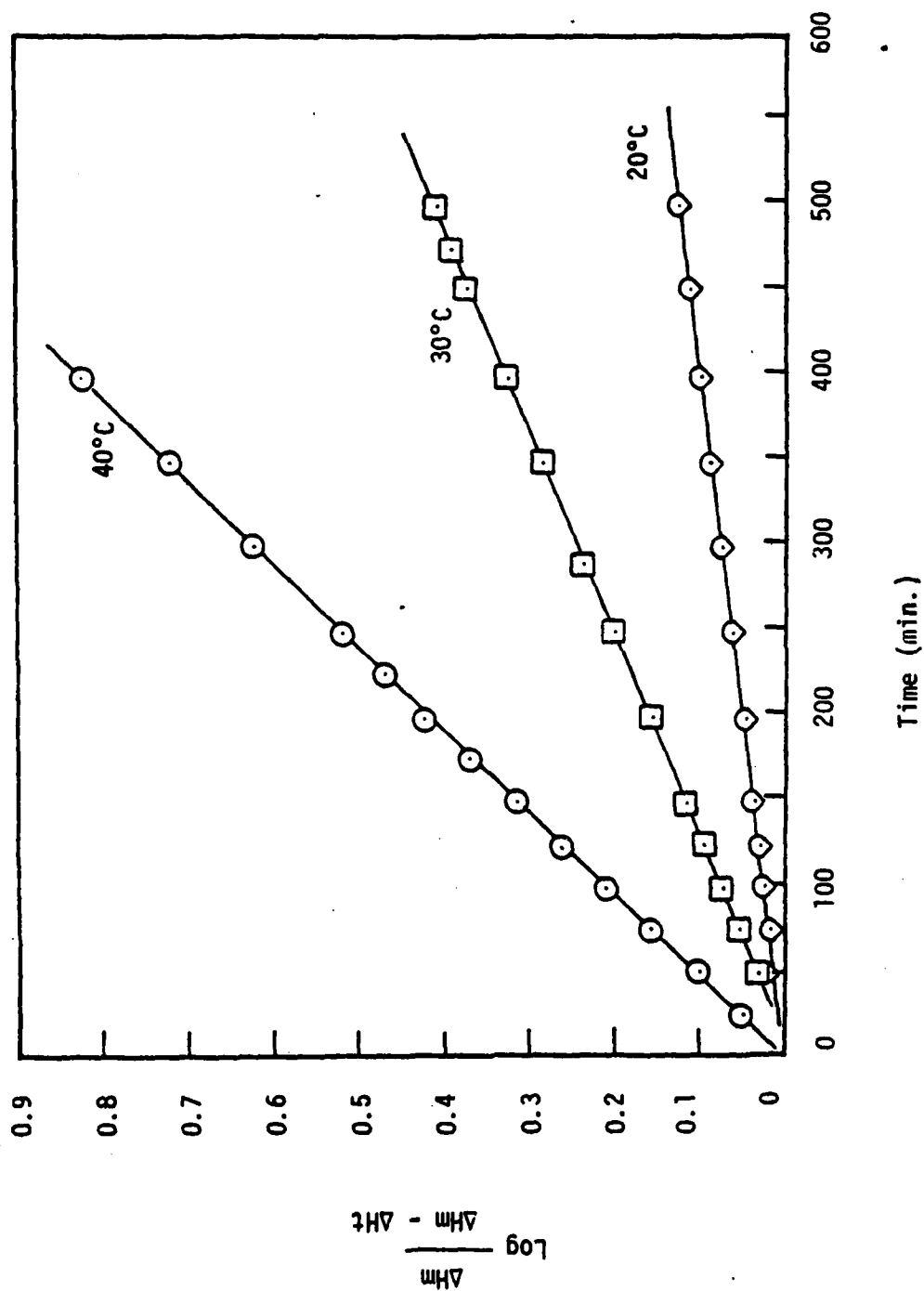


Figure 3. First-Order Plots for Butadiene in Hexane

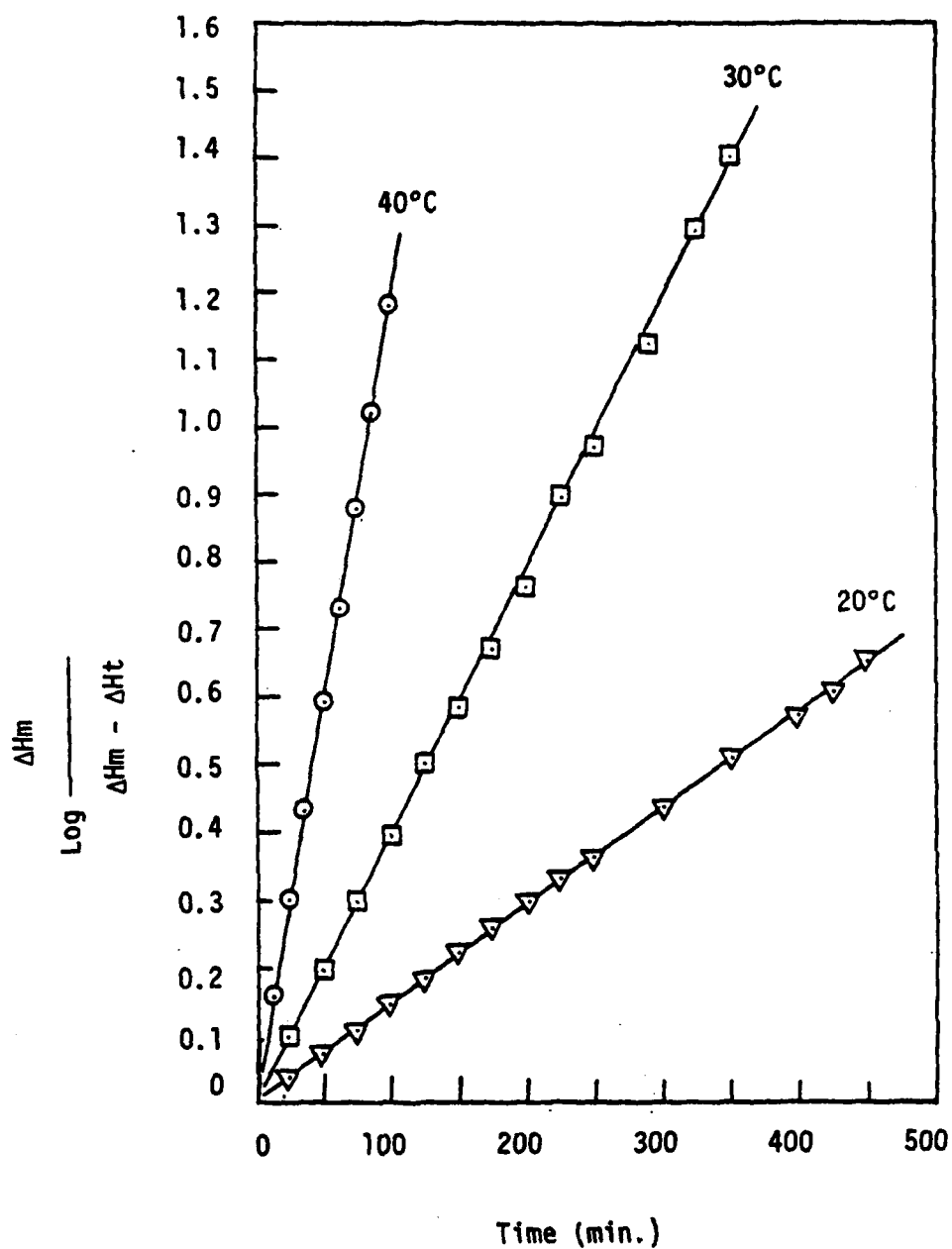


Figure 4. First-Order Plots for Isoprene in Hexane

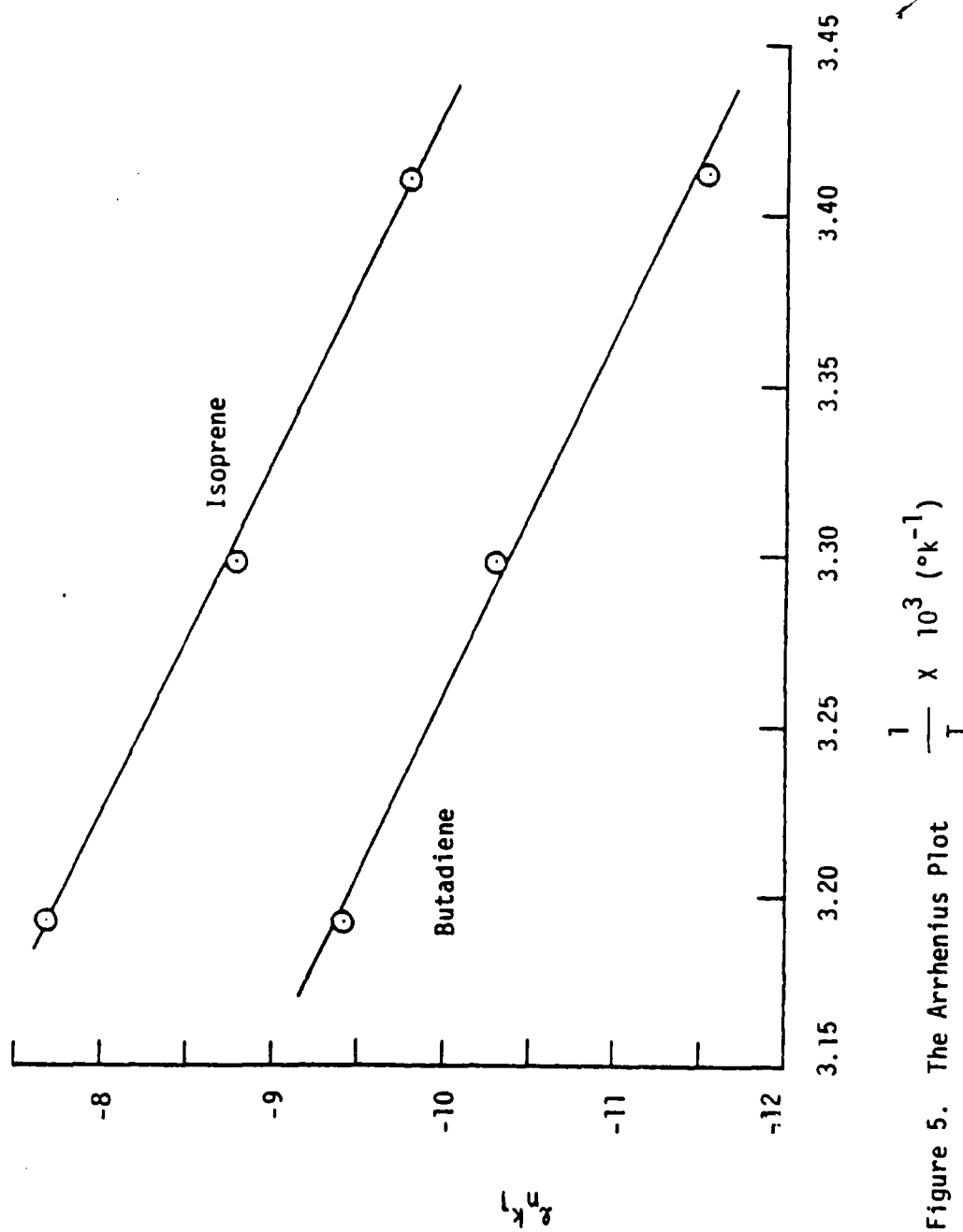


Figure 5. The Arrhenius Plot

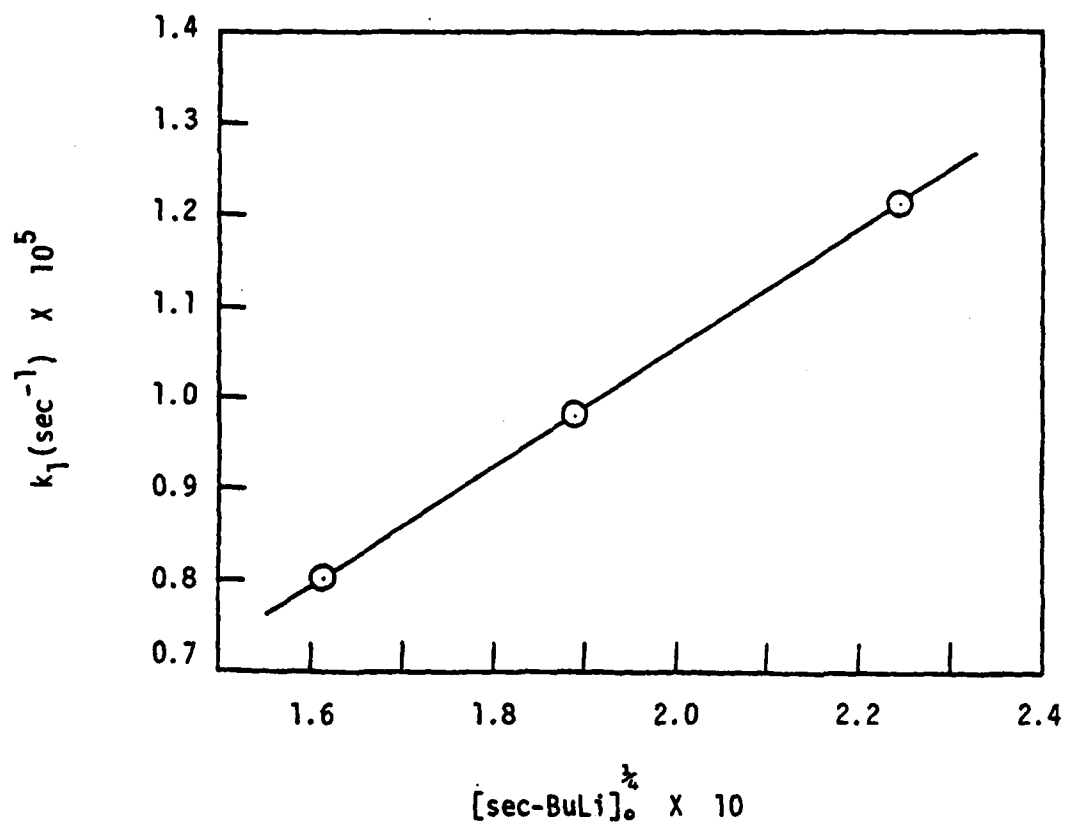


Figure 6. Dependence of Butadiene Rate on Initiator Concentration in Hexane at 20°C

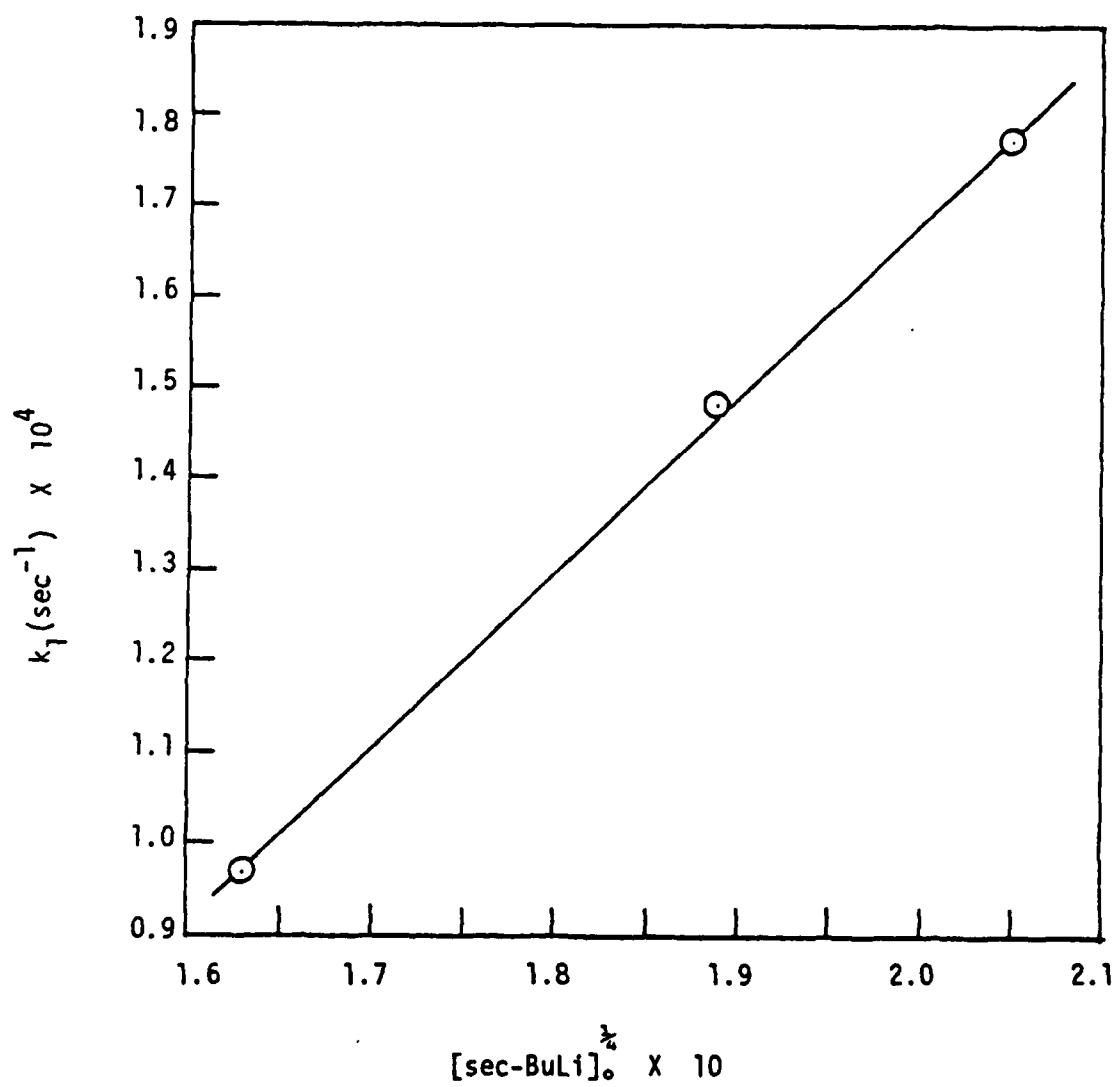


Figure 7. Dependence of Isoprene Rate on Initiator Concentration in Hexane at 30°C

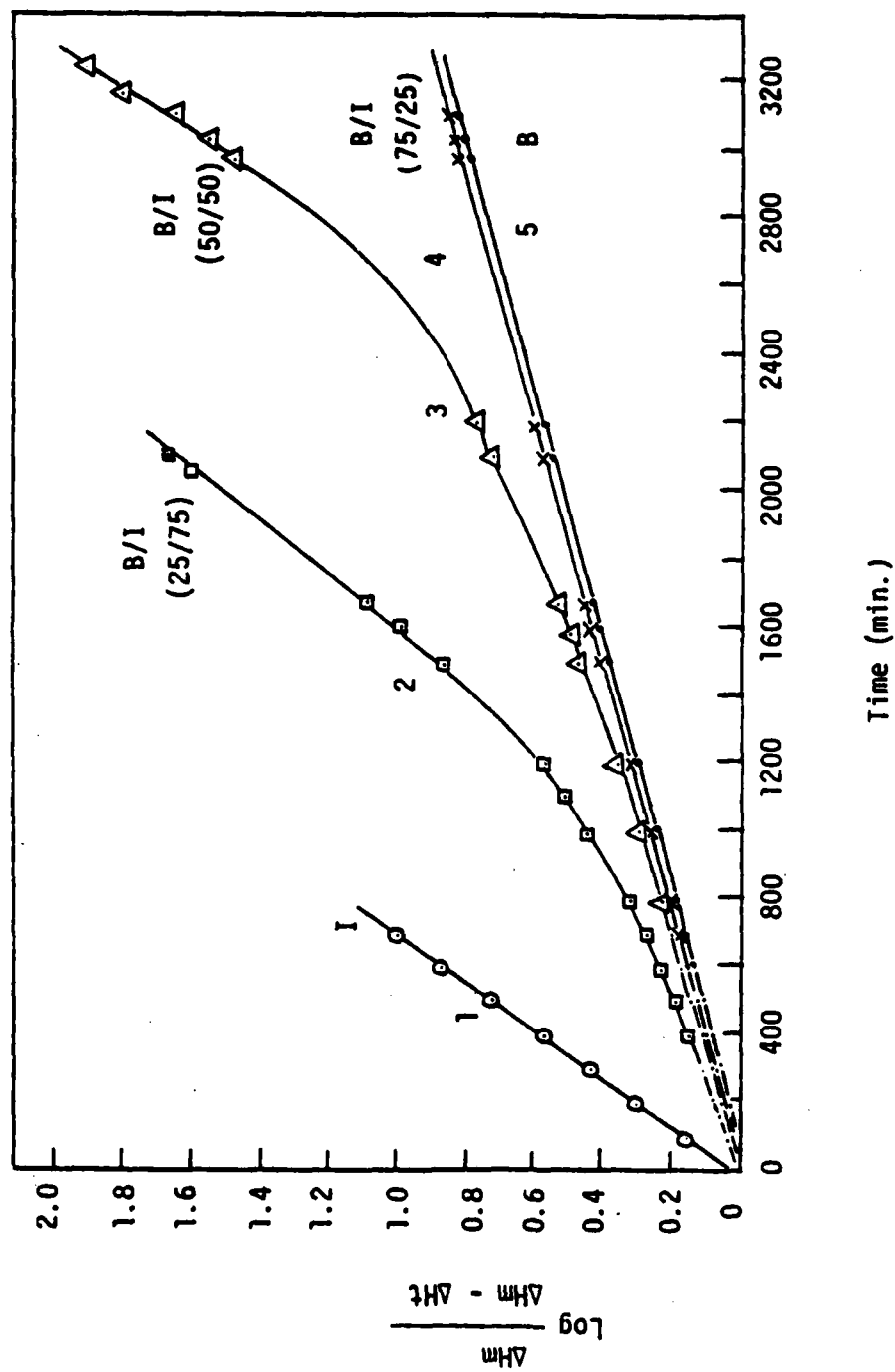


Figure 8. Effect of Comonomer Feed Ratio on the Rate of Polymerization in Hexane at 20°C

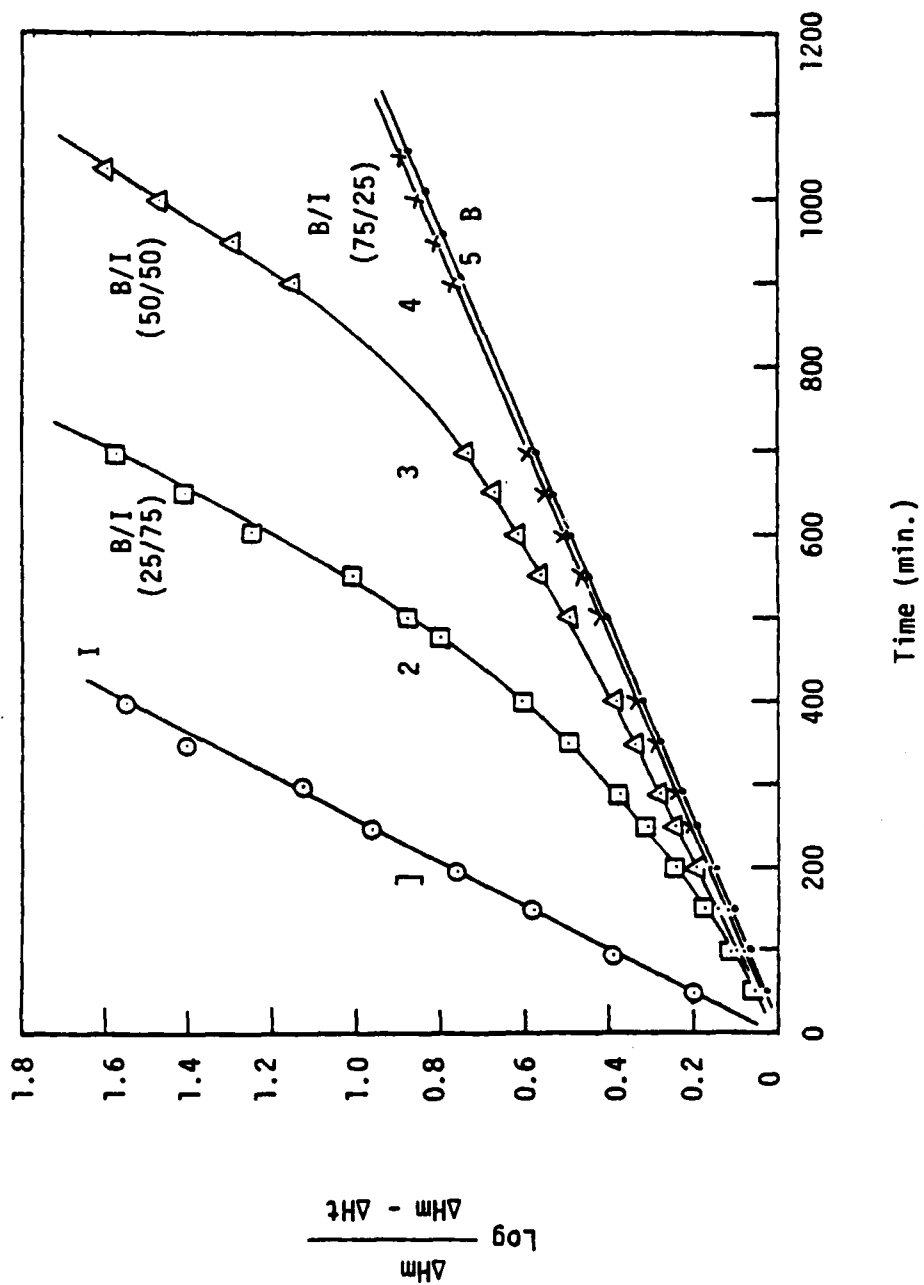


Figure 9. Effect of Comonomer Feed Ratio on the Rate of Polymerization in Hexane at 30°C

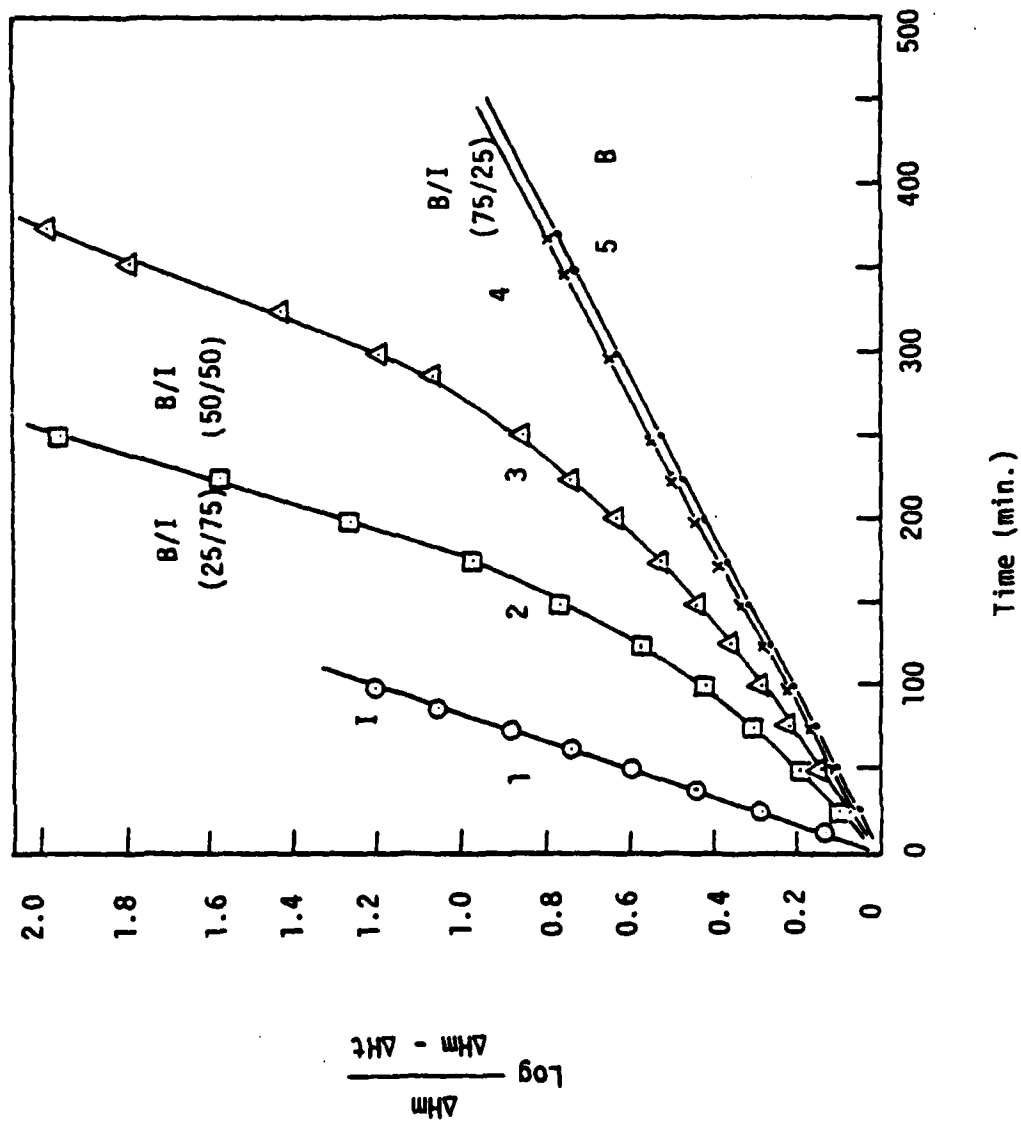


Figure 10. Effect of Comonomer Feed Ratio on the Rate of Polymerization in Hexane at 40°C

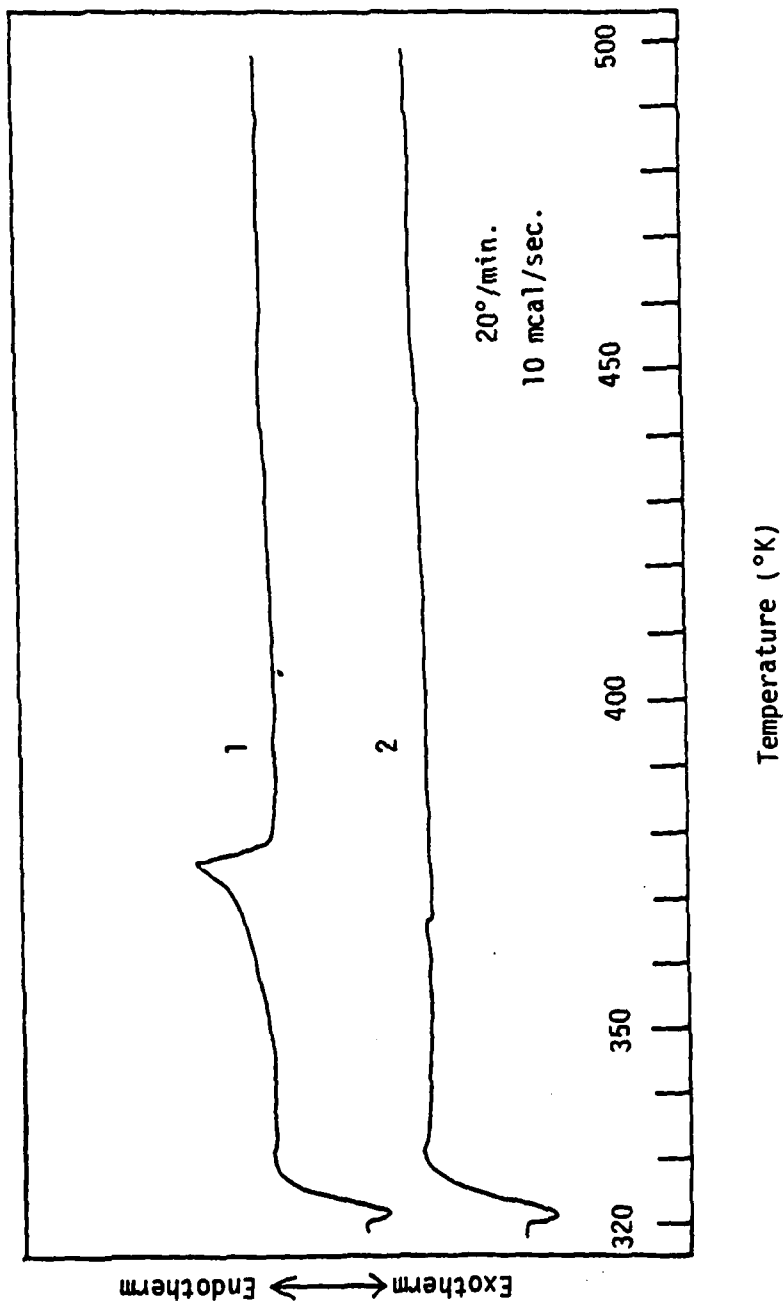


Figure 11. DSC diagrams of totally hydrogenated derivative of (1) diblock copolymer, 9-ICW-29, by sequential addition of monomers with wt. % of PB/PI of 49/51; and (2) copolymer, 9-ICW-88, by direct addition of monomers with wt. % of PB/PI of 48.8/51.2.

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II. The Reactivity of Polydiene Anions with Divinyl Benzene.

THE REACTIVITY OF POLYDIENE ANIONS WITH DIVINYLBENZENE

by

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SYNOPSIS

Star-branched homopolymers of butadiene and isoprene have been synthesized utilizing anionic polymerization techniques. The commercial mixture of divinylbenzene was employed as the star linking agent for the "living" polydienyllithium anions. The nature of the star-branching reaction was studied with respect to: the molar ratio of divinylbenzene (DVB)/Alkylolithium (RLi), reaction temperature, reaction time and the nature of the polydienyllithium chain end. In general, a higher number of arms is achieved via increased DVB/RLi ratio, reaction temperature and through the choice of polybutadienyl chain ends.

The polymers were characterized by gel permeation chromatography (G.P.C.), membrane osmometry, intrinsic viscosity, and H-NMR spectroscopy. A Chromatix low-angle light scattering G.P.C. detector was also employed for the determination of the weight average molecular weight (\bar{M}_w), as well as a sensitive detector, in order to assay absolutely the \bar{M}_w versus elution volume profile for a series of star-branched polyisoprenes and polybutadienes. The results indicate that under optimum conditions a relatively well defined number of arms can be achieved with DVB linking.

INTRODUCTION

In 1965, Milkovich¹ reported that divinylbenzene could be utilized for the formation of star-branched macromolecules. Later, Rempp and co-workers²⁻⁴ successfully applied this method for the synthesis of star-branched polystyrenes. Moreover, Fetters and coworkers⁵⁻⁸ used this

procedure for the synthesis of multi-arm star-branched polyisoprene homopolymers and polystyrene-polydiene block copolymers. This method of star-branched polymer formation involves the sequential polymerization of monomer giving the "arm", followed by the addition of divinylbenzene. The polymerization of divinylbenzene then results in a "microgel" nucleus containing pendant vinyl groups which serve as branch points for the star-shaped polymer. This procedure has led to the formation of star-branched polyisoprenes containing up to 56 weight-average numbers of arms.^{5,6} The arms of these star macromolecules possess narrow molecular weight distributions due to the termination free aspect of diene polymerizations initiated by organolithium species in hydrocarbon solvents.⁹

Star-branched block and homopolymers are of interest both from a theoretical and practical viewpoint. Studies on the melt rheology have shown the viscosity to be independent of the extent of branching, yet dependent upon the arm molecular weight.^{6,8} Star-branched styrene-butadiene block copolymers appear to have improved mechanical properties and processability over the linear styrene-butadiene-styrene analogs.^{7,8} A high styrene content star-shaped block copolymer introduced by Phillips (K-resin) offers the rigidity, transparency, and good impact strength necessary for packaging and thermoforming applications.¹⁰ High butadiene content star block copolymers have been used in hot melt and pressure sensitive adhesives.^{11,12} Due to this growing interest in star-branched polymer behavior, it became of interest to study the nature of the star-branching reaction between polydienyllithium anions and the commercial mixture of divinylbenzene. The subject of our research discussed herein was to investigate the variables that influence the star formation process.

These certainly include the molar ratio of DVB/RLi, the linking reaction temperature, reaction time, and the nature of the "living" diene chain end.

EXPERIMENTAL

Star-polymer synthesis was achieved by utilizing an all glass high vacuum design as shown in (Figure 1). Monomers and solvents were purified by drying over calcium hydride; with periodic degassing, followed by distillation under vacuum over a succession of sodium mirrors. The commercial DVB monomer was further purged over dibutylmagnesium, which produced a bright-yellow complex that was indicative of dryness. Solvents and diene monomer were further stored over an organometallic purge until needed. The DVB was split down into ampoules in benzene or hexane to form 0.2N-0.8N solutions. This was necessary due to the high reactivity of DVB.

A typical polymerization reactor is shown in (Figure 2). The reactor contains a side-ampoule used to isolate a portion of the "living" linear precursor before star-linking by the addition of DVB. The reactor was purified by flaming with a hand torch while continuously pumping until a pressure of 10^{-5} torr was reached. The apparatus was then heat-sealed from the vacuum line via the constriction and the interior walls of the reactor rinsed with n-butyllithium-hexane solution in order to remove any adsorbed impurities on the interior walls of the glassware.

Sec-Butyllithium was used as the initiator to prepare the polydienes. The sec-butyllithium was purified by high vacuum distillation as described in previous work.¹³ The pure sec-butyllithium was then diluted with hexane and split-down into ampoules containing breakseals. Each ampoule could be used for subsequent polymerization. A typical split-down apparatus is shown in (Figure 3). Initiator concentrations were determined by titration

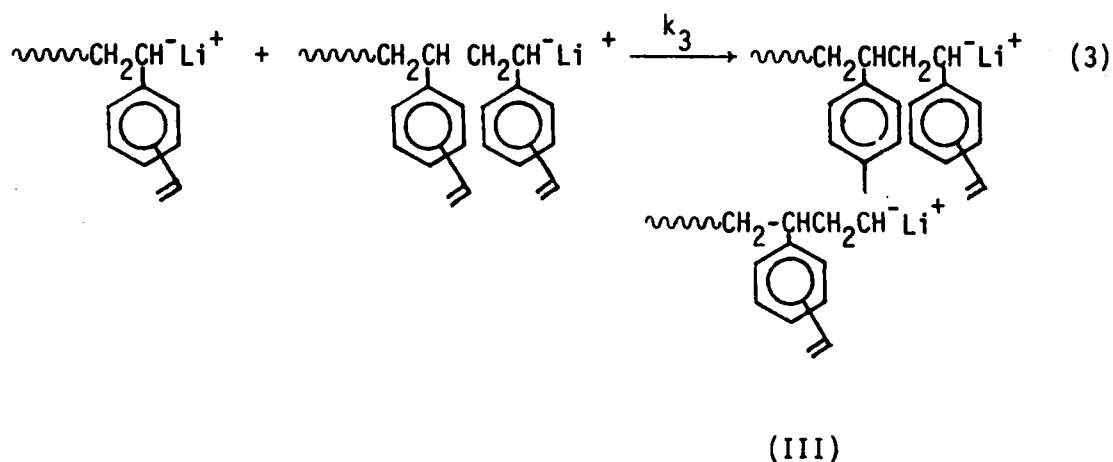
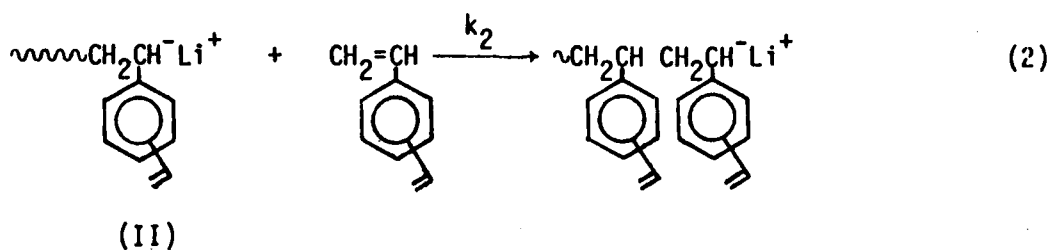
with standard HCl to a phenolphthalein endpoint.

The diene polymerizations were generally allowed to proceed for 48 hours, which ensured quantitative conversion. In the case of butadiene, the reactor was cooled periodically to draw residual butadiene monomer into the solution from the void volume of the reactor.

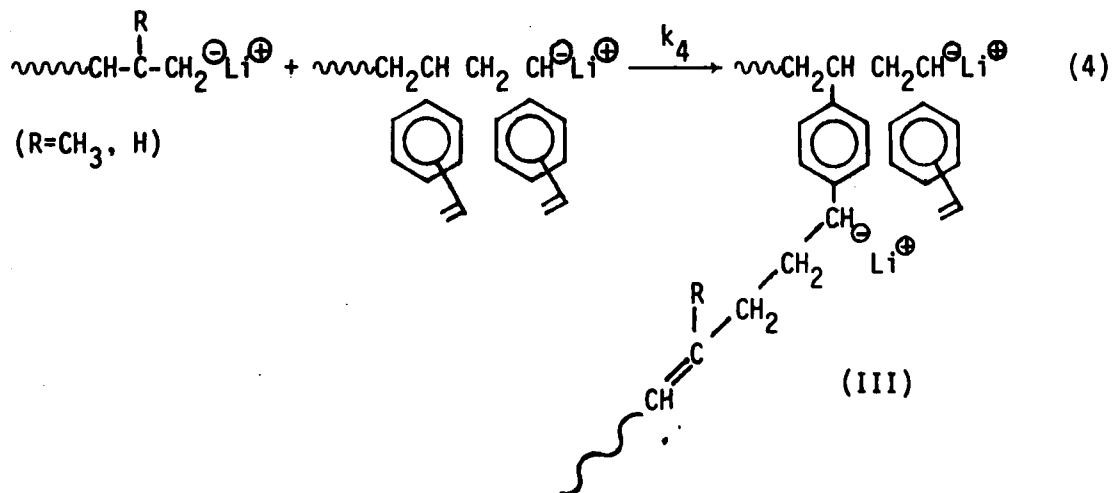
The star-shaped polymers were prepared by the addition of the DVB solution to the "living" polydienyllithium hexane solution. Prior to the addition of divinylbenzene (DVB), a portion of the linear polymer solution was isolated via the sidearm, which enabled the arm molecular weight to be determined.

Upon addition of divinylbenzene the characteristic red-orange color of the styryllithium type anion resulted. After the star-polymer formation was complete, the solutions were terminated with degassed methanol. The polymer was precipitated in methanol and dried to a constant weight under vacuum. Characterization techniques included membrane osometry, intrinsic viscosity, GPC and spectroscopic methods. A Wescan recording osmometer was used at 43°C with chlorobenzene as the solvent. The accuracy of the instrument was checked by the use of several solutions of known molecular weight polystyrene standards. The values of \bar{M}_n were determined from measurements made on solutions of at least four concentrations, followed by the typical $(\pi/c)^{1/2}$ versus concentration plot procedure. The gel permeation chromatography analysis was achieved using a Waters HPLC equipped with both refractive index and U.V. detectors. The carrier solvent was tetrahydrofuran at 25°C, with a flow rate of 1.0ml/min. The column arrangement consisted of four one-ft. columns of microstysragel with a continuous porosity range of 500 Å, 10^3 Å, 10^4 Å, and 10^5 Å.

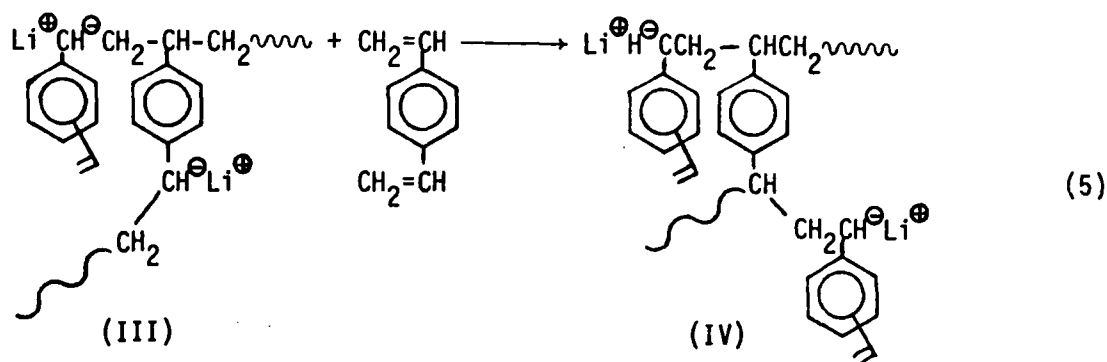
Once the vinylbenzyl anion (II) forms, it may add to another divinylbenzene molecule resulting in DVB "homopolymerization" (Reaction 2). Likewise, the vinylbenzyl anion (II) may attack a pendant vinyl group of another polymer chain (Reaction 3) to give the alkylbenzyl anion (III).



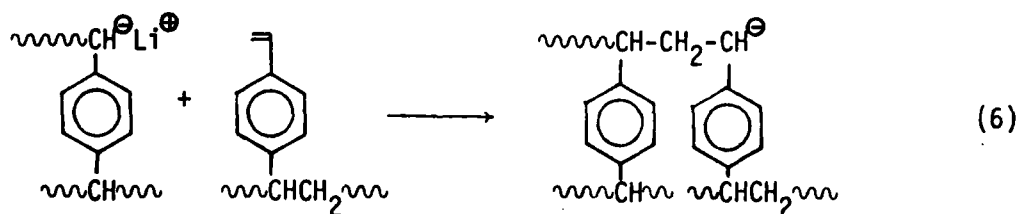
In analogous fashion, an uncapped polybutadienyllithium or polyisoprenyllithium anion may attack an unreacted pendant vinyl group of another polymer chain (Reaction 4) to give the alkylbenzyl anion (III).



Reactions (3) and (4) described above result in the beginning of star-branched polymer formation. Once the alkylbenzyl anion (III) has formed it may further react with any available DVB monomer as illustrated in reaction sequence (5).



Reaction 5 above would be more probable at the higher molar ratios of DVB/RLi. Finally, in the latter stages of the star formation process, the remaining residual vinyl groups would react as illustrated in (Reaction 6).



The reaction sequences described above are simplified, since "living" chain end self-association and cross-association will further complicate the reaction.

As seen from the above reaction steps, the DVB procedure for star-branched polymer formation consists of several competitive and consecutive reactions. It was the aim of our work to study various reaction variables which effect this process. As mentioned earlier, these include:

DVB/RLi molar ratio, reaction temperature, reaction time, and the nature of the "living" diene chain end. In the ensuing discussion, we will describe how these above mentioned factors influence the efficiency of the star-formation process.

INFLUENCE OF THE DVB/RLi MOLAR RATIO

By using various molar concentrations of sec-butyllithium and DVB, the effect of the DVB/RLi ratio was investigated on these star-branched polymerizations. First, butadiene was distilled into a known concentration of a sec-butyllithium hexane solution. The homopolymerization of butadiene was carried out for 48 hours and the polymer analyzed by G.P.C.; a typical G.P.C. chromatogram is shown in (Figure 4). One can observe the narrow distribution (\bar{M}_w 1.07) and the peak height elution volume at 29 ml. The DVB solution was then added via the break-seal into the polybutadienyl-lithium solution at 25°C. The yellow-orange color developed, indicative of the cross-over reaction. The star-branching was allowed to proceed for 72 hours after which the polymer was isolated. The G.P.C. chromatogram of the resulting polymer is shown in (Figure 5). One notices a considerable portion of "unlinked" material with an elution volume at 27 ml. The linear precursor, however, had a peak elution volume at 29 ml. From the G.P.C. analysis it was concluded the polymer fraction eluting at 27 ml. was a coupled dimer or two-arm star. The DVB/RLi ratio in this case was 3.0 (corrected for 44% EVB). From this observation it became of interest to study the influence of DVB/RLi ratio on the efficiency of star formation. The reaction time, temperature, and arm molecular weight were held constant while the DVB/RLi ratio varied.

Figure 6 illustrates the effect of the DVB/RLi ratio. It was observed that as the DVB/RLi ratio increased, the percentage of unlinked lin-

ear material decreased. At the lower DVB/RLi ratios, linear coupled two arm stars were formed, while at the higher ratios, the linear material was not coupled. Thus, there is a strong influence on the efficiency of the star-branched polymer formation as the DVB/RLi ratio is varied for the case of poly(butadienyllithium). At the low molar ratios of DVB/RLi and two arm coupling reaction competes with the star-formation process.

Figure 7 illustrates the influence of the increase in the DVB/RLi ratio as well as reaction time for polybutadienyllithium anions. The efficiency is plotted as the ratio of linked to unlinked chains. At the very high ratios (21-23) nearly quantitative linking is observed as seen from the G.P.C. analysis in Figure 8. However, the molecular weight distribution is broadened at the higher ratios, possibly indicating inter-molecular or inter-nodule star coupling between two different star macromolecules. As mentioned previously, Reaction 5 would be more likely to occur at the higher ratios; thus the overlap of the vinylbenzyl anion of the polymer chain to that of adjacent "living" star nodule would result in inter-star coupling. A broadened G.P.C. curve may be observed by using the Chromatix low angle laser light scattering detector (LALLS). One advantage this detector offers is its high sensitivity to high molecular weight species. As observed in Figure 9, the weight average molecular weight elution volume profile shows a shoulder at the high molecular weight end of the chromatogram. This shoulder reflects the percentage of inter-nodule coupling observed at the higher DVB/RLi ratio. This shoulder also reflects an inconsistency in the relationship of molecular weight to hydrodynamic volume. In other words, an increase in the eluant molecular weight is observed with increased molecular branching or it may be related to the

column exclusion limit. Inter-nodule coupling gives increased branching along with increased molecular weight as evidenced by the Chromatix LALLS analysis.

For polyisoprenyllithium anions, it was also observed that increased linking efficiency was achieved at higher DVB/RLi ratios (Figure 10). In comparison, the polyisoprenyllithium anions link more efficiently than polybutadienyllithium. Also, in contrast to polybutadienyllithium anions, polyisoprene star formation does not result in coupled dimer at the lower DVB/RLi ratios. This is perhaps reflected in the faster cross-over rate from the polydienyllithium anion to the vinylbenzyl anion (reaction 1) for polyisoprene.

The reaction temperature was also found to influence the efficiency of the linking reaction. As summarized in Table I, the increase in reaction temperature from 25°C to 45°C resulted in an increase in star-branch polymer formation. Qualitatively, it was also observed that the formation of vinylbenzyl anion occurred more rapidly at the elevated temperatures. Apparently, the increased reaction temperatures render the intermolecular attack on the pendant vinyl groups by the polydienyllithium anions more favorable in comparison to the intramolecular intra-nodule alkylbenzyl anion-vinyl group reaction. (Table I on the following page).

From the summary in Table I, it can be seen that increased reaction temperatures lead to more rapid and efficient linking, when compared to the reactions carried out at 25°C.

Comparing samples in Table I (4-MM-S-17, a-e), one observes that increasing the reacting time also results in more quantitative linking. However, the percent of further increased linking is smaller at longer reaction times. As the "living" star nodule continues to react, increased steric hindrance slows down the ability of a macromolecular carbanion to enter into the "microgel" nodule.

TABLE I
POLYBUTADIENE STAR POLYMERS

Sample	DVB/RLi ^(a)	\bar{N}_a ^(b)	% Linear ^(c)	Reaction Time (HRS)	T°C	Solvent
2-MM-S-1	5.4	18	360 ^(d)	72	25°C	Hexane
2-MM-S-5	10.6	--	29 ^(e)	24	45°C	Hexane
2-MM-S-6	8.8	15	6	36	45°C	Hexane
2-MM-S-7	5.7	23.4	21.90	48	45°C	Hexane
2-MM-S-8	5.0	13.4	25.70	56	45°C	Hexane
3-MM-S-12	21.6	16	1	48	50°C	Benzene
3-MM-S-13	23.0	--	2	24	50°C	Benzene
3-MM-S-15	12.2	23.8	5.9	72	50°C	Hexane
4-MM-S-17a	7.2	--	33.1	6	25°C	Benzene
4-MM-S-17b	7.2	--	13.8	24	25°C	Benzene
4-MM-S-17c	7.2	--	4	152	25°C	Benzene
4-MM-S-17d	7.2	--	2.4	163	25°C	Benzene
4-MM-S-17e	7.2	--	1.7	200	25°C	Benzene

(a) DVB/RLi ratio includes 44% ethylvinylbenzene present in the commercial DVB.

(b)
$$\bar{N}_a = \frac{\bar{M}_n \text{ Star}}{\bar{M}_n \text{ Linear}}$$

(c) % linear from G.P.C.

(d) D represents coupled dimer

(e) It is suspected some premature termination resulted for 2-MM-S-5.

From the data in Tables I and II, one observes an increase in the DVB/RLi ratio does not necessarily result in more highly branched star-shaped polydienes. In other words, an increase in the DVB/RLi ratio results in more quantitative star formation but not always increased branch functionality.

In comparison to the polybutadiene stars under similar reaction conditions, the polyisoprene stars showed slightly lower degrees of branching. The added steric hindrance from the methyl group on the polyisoprene anion perhaps makes entry into the DVB "microgel" nodule difficult.

TABLE II
POLYISOPRENE STAR POLYMERS

Sample	DV/RLi ^(a)	\bar{N}_a ^(b)	%Linear ^(c)	Reaction Time (hrs.)	Temp. (°C)	Solvent
2-MM-S-2	5.4	7.7	23%	14	25°C	Hexane
2-MM-S-3	10.8	13.1	6%	62	25°C	Hexane
2-MM-S-4	12	9.8	5%	96	25°C	Hexane
2-MM-S-9	9.5	12.7	3%	62	45°C	Hexane
2-MM-S-10	5.8	9.8	8.5%	62	45°C	Hexane
3-MM-S-16	21.2	12.1	9.8%	48	50°C	Benzene

(a) DVB/RLi includes 44% Ethylvinylbenzene present in commercial DVB.

(b) $\bar{N}_a = \frac{\bar{M}_n \text{ star}}{\bar{M}_n \text{ arm}}$

(c) Determined from G.P.C.

TABLE III
CHROMATIX LASER LIGHT SCATTERING GPC SUMMARY

Sample	Light-Scattering		Osmotic	(\bar{M}_w/\bar{M}_n) l.s.		(\bar{M}_w/\bar{M}_n) o.p.	DVB/RLi ^(c)
	\bar{M}_n	\bar{M}_w (b)	\bar{M}_n				
PI-S-16	422,641	563,200	458,000	1.33	1.23		21.2 (11.9)
PI-S-16	446,000	610,430	458,000	1.37	1.33		21.2 (11.9)
PI-S-9	521,100	574,982	521,800	1.10	1.10		9.5 (5.3)
PB-S-15	833,700	865,257	--	1.04	--		12.2 (6.8)
PB-S-8	468,184	486,358	549,500	1.04	--		5.0 (2.8)

(DN/DC) = 0.1407 PI/THF 25°C (DN/DC) = 0.1398 PI/THF 25°C

(a) $\bar{M}_n = \frac{\sum C_I}{\sum \frac{C_I}{M_I}}$ (b) $\bar{M}_w = \frac{\sum C_I M_I}{\sum C_I}$ (c) Values in parentheses are corrected for 44% ethylvinylbenzene

LALLS ANALYSIS

The Chromatix¹⁴ low angle laser light scattering (LALLS) G.P.C. detector was employed for further analysis of a few star-shaped polydienes. The unique feature of the (LALLS) detector is its high sensitivity to the high molecular weight fractions within the molecular weight distribution. The LALLS detector is also able to measure the weight average molecular weight (\bar{M}_w) as a function of elution volume from the G.P.C. Thus, the "universal" calibration procedure is not required. Table III summarized the LALLS results. From these results, it can be concluded that higher DVB/RLi ratios result in broader molecular weight distributions. As described previously, this is due to an increased amount of inter-nodule linking between two growing star-shaped molecules. The light-scattering \bar{M}_n values agree with those determined independently from membrane osmometry measurements.

STAR-POLYMER CHARACTERIZATION

Characterization was achieved by using a Waters Gel Permeation chromatograph. The \bar{M}_n molecular weight characterization was achieved by membrane osmometry. Table IV summarizes the G.P.C. as well as the membrane osmometry results. The elution volume behavior for the star-branched materials appear insensitive to the overall star-branched polymer molecular weight, while more dependent upon arm molecular weight. This is what one might expect as the G.P.C. separation process occurs by differences in hydrodynamic volume not actual molecular weight. As the star-branched arm molecular weight increases so does the hydrodynamic volume, hence earlier elution volumes would be expected with increasing arm molecular weight.

TABLE IV

Sample	\bar{M}_n Linear Precursor	\bar{M}_n Star	Elution Volume	
			Star	Linear
Polybutadiene				
2-MM-S-1	32,000	589,000	24.2 ^(a)	29
2-MM-S-6	64,000	959,000	22.7	27
2-MM-S-7	35,200	824,400	22.1	26.2
2-MM-S-8	34,800	614,000	22.1	26.0
3-MM-S-12	35,000	562,000	22.1	26.2
3-MM-S-15	35,000	833,700	22.0	26.2
Polyisoprene				
2-MM-S-2	27,550	211,500	24.5	28.3
2-MM-S-3	51,000	673,000	23.6	27.5
2-MM-S-4	55,700	562,000	23.5	27.6
2-MM-S-9	41,150	521,800	23.8	27.9
2-MM-S-10	39,800	389,000	24	28.0
3-MM-S-16	37,700	458,000	22 ^(b)	27.1

(a) GPC column set different for sample S-1

(b) GPC column set different for sample S-16

CONCLUSION

Star-branched poly(butadienes) and poly(isoprenes) have been synthesized by linking the "living" chain ends with commercial DVB. Higher DVB/RLi molar ratios result in a more efficient star-branching process. DVB/RLi molar ratios greater than 10-11 give nearly quantitative linking; however, these star-branched polymers have higher polydispersity ratios (e.g. $\overline{\overline{M}}_w/\overline{\overline{M}}_n = 1.3$). This can be rationalized by an increased probability of intermolecular star-nodule coupling result in a high molecular weight fraction within the molecular weight distribution. Increased reaction times and temperatures likewise give more quantitative linking for a given DVB/RLi molar ratio.

The star-formation process was also found to be sensitive to the nature of the "living" polydienyllithium chain end. Polybutadienyllithium anions cross-over to give the vinylbenzyl anions, upon reaction with DVB, at a slower rate than the corresponding polyisoprenyllithium anions. Furthermore, it was observed that when low DVB/RLi ratios were employed to link polybutadienyllithium anions, that a two-arm coupling reaction resulted, in effective competition with star-branched polymer formation. However, in the case of polyisoprenyllithium anions no such dimerization was observed under similar linking reaction conditions. This can perhaps be reflected in the overall faster cross-over reaction of polyisoprenyllithium chain ends with DVB as compared to the corresponding reaction for polybutadienyllithium.

Low Angle Laser Light Scattering (LALLS) results indicate, that at lower DVB/RLi molar ratios, a relatively narrow molecular weight distribution (1.04-1.1) of star-branched polymers can be synthesized. In contrast, DVB/RLi ratios greater than 11 can lead to rather broad molecular weight distributions ($\overline{\overline{M}}_w/\overline{\overline{M}}_n = 1.3$).

It is not certain how the ethylvinylbenzene isomers influence the star-formation process and further experiments are necessary. The influence of reaction temperature on the stability of the vinylbenzyl and polydienyllithium chain ends is presently under investigation utilizing U.V.-visible spectroscopic techniques. Future experiments are in progress⁽¹⁶⁾ to further advance the existing knowledge of this interesting polymerization process.

Fig. 1

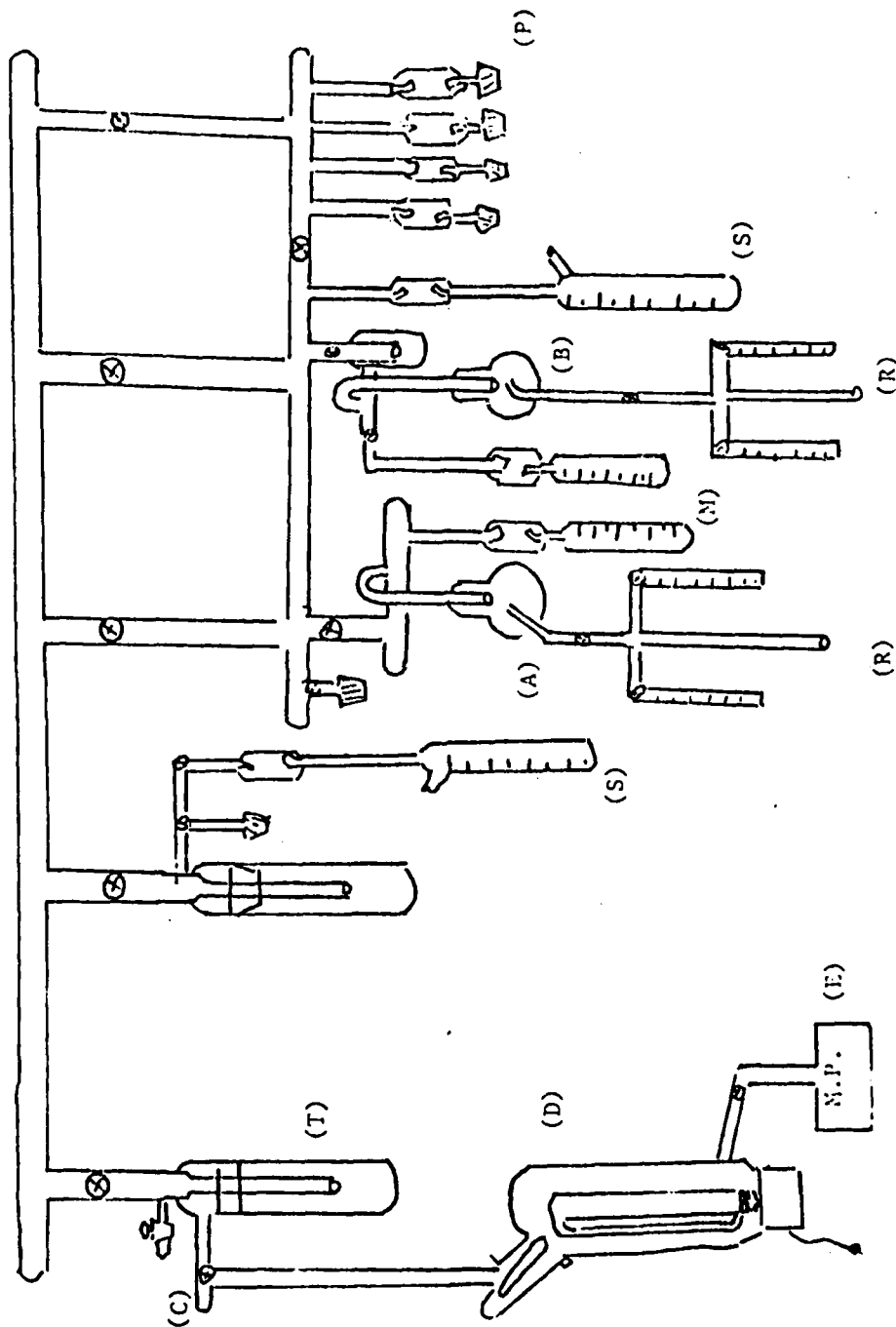


Figure 7. High Vacuum Apparatus.

7.9.2.

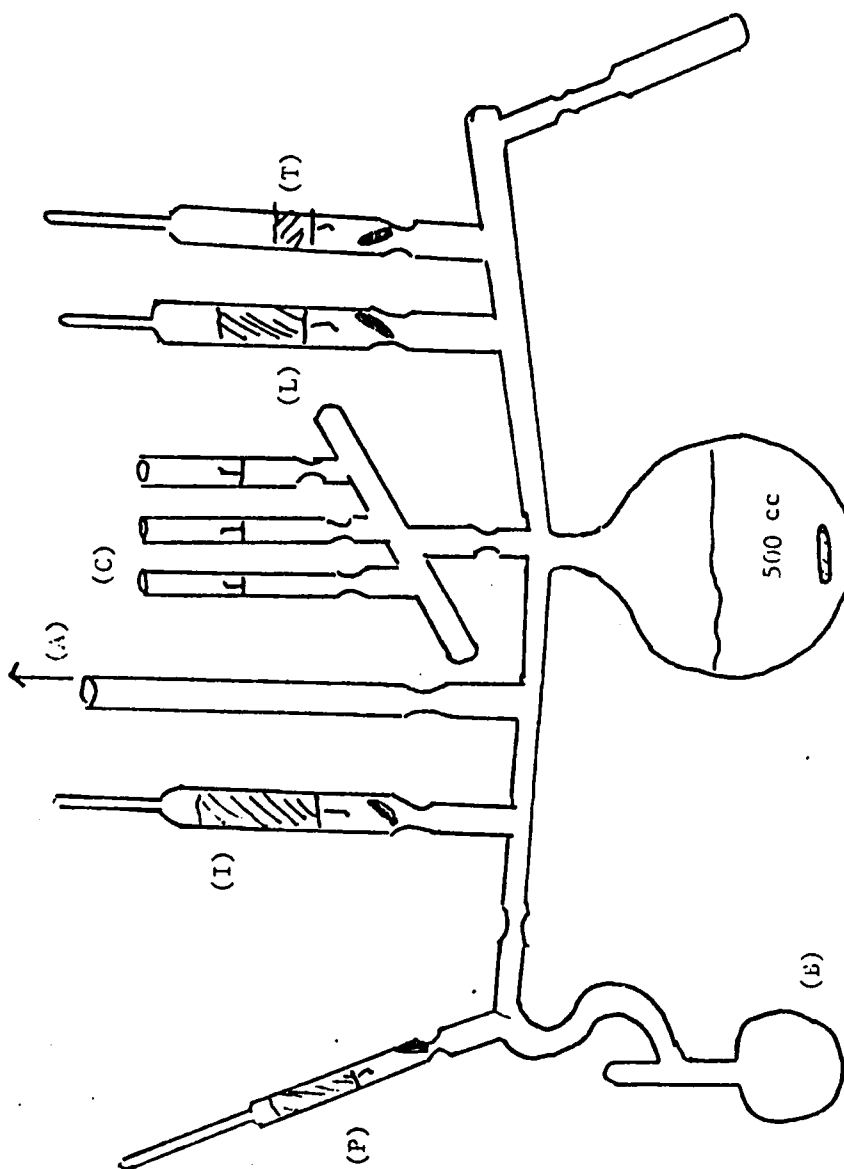


Figure 15. Polymerization Reactor.

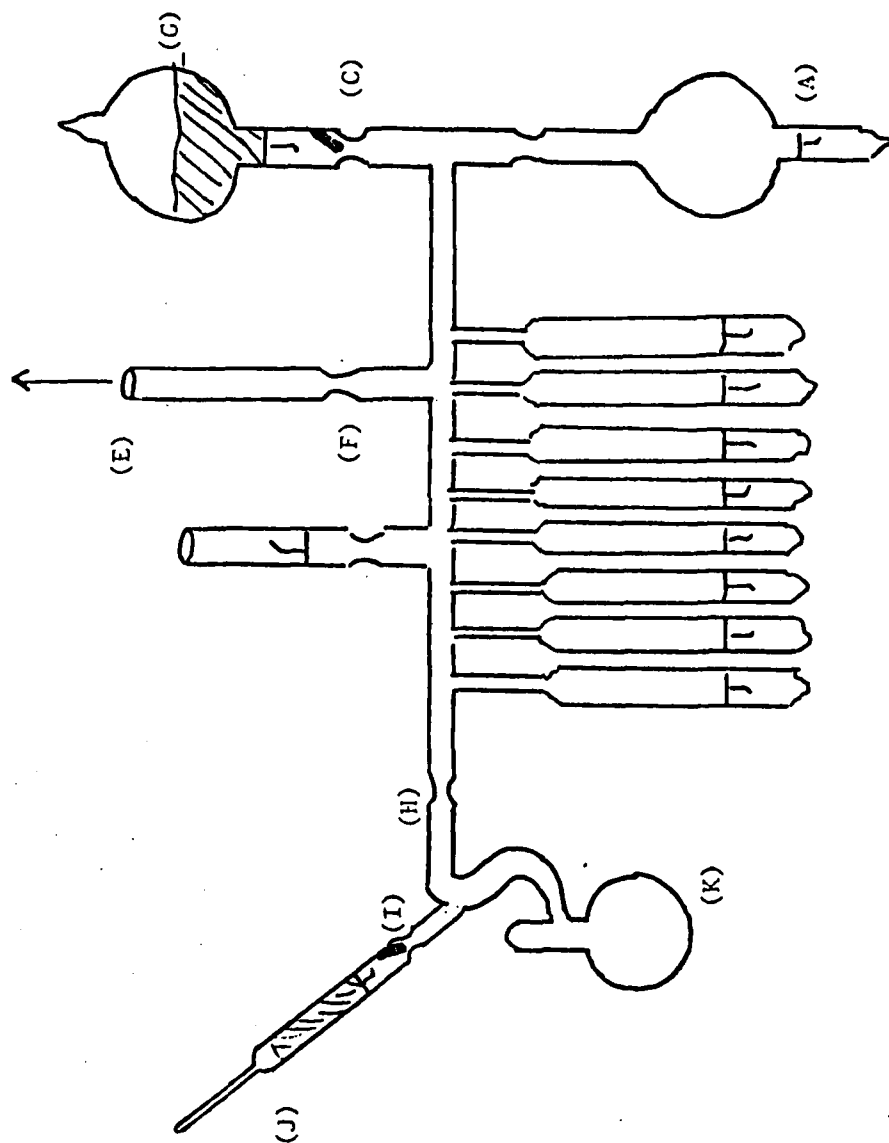


Figure 14. sec-Butyllithium Split-down Apparatus.

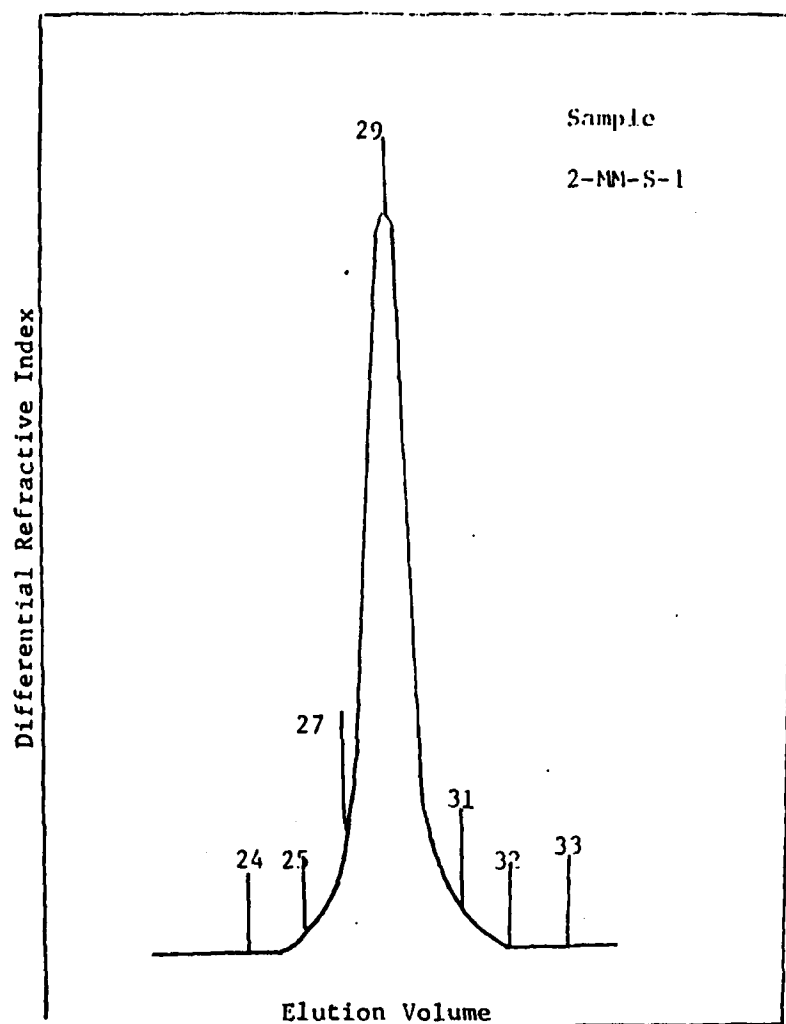


Figure 21. G.P.C. Chromatogram of Linear Precursor

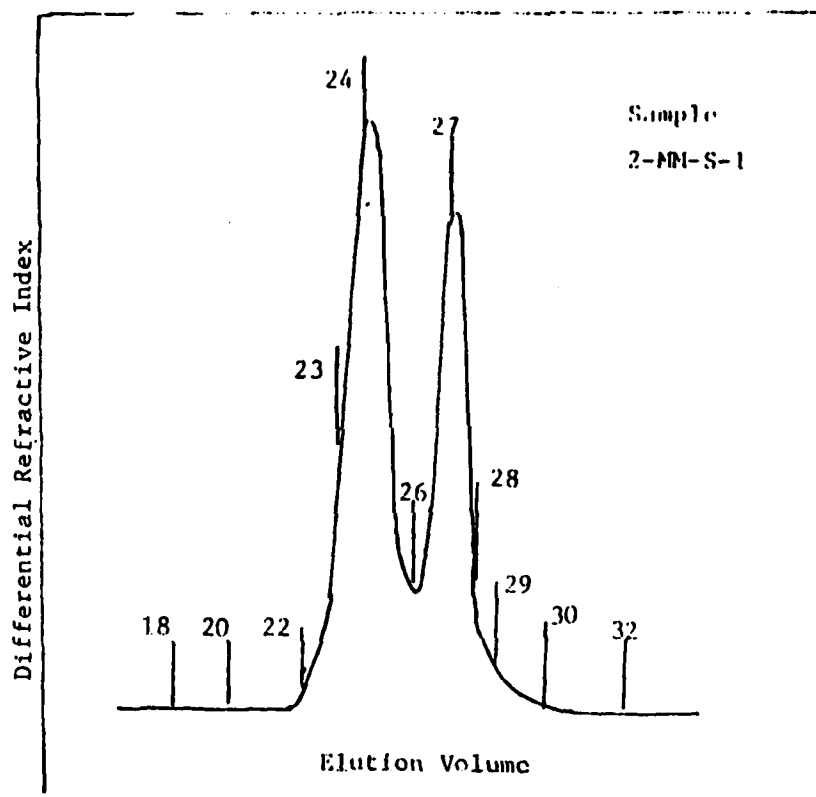


Figure 22. G.P.C. Chromatogram of Star-branch Poly(butadiene) Linked for 72 hrs. at 25°C.

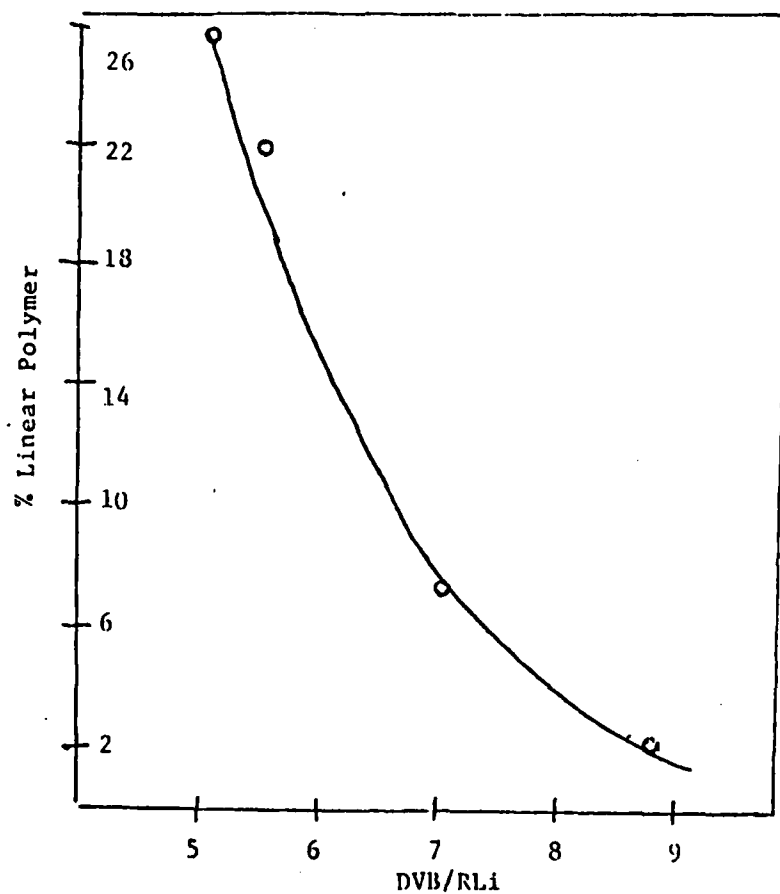


Figure 23. % Linear Polymer vs. DVB/RLi Ratio
for Poly(butadiene) Anions Linked
With DVB at 45°C for 48 hrs.

(\bar{M}_n arm = 35,000)

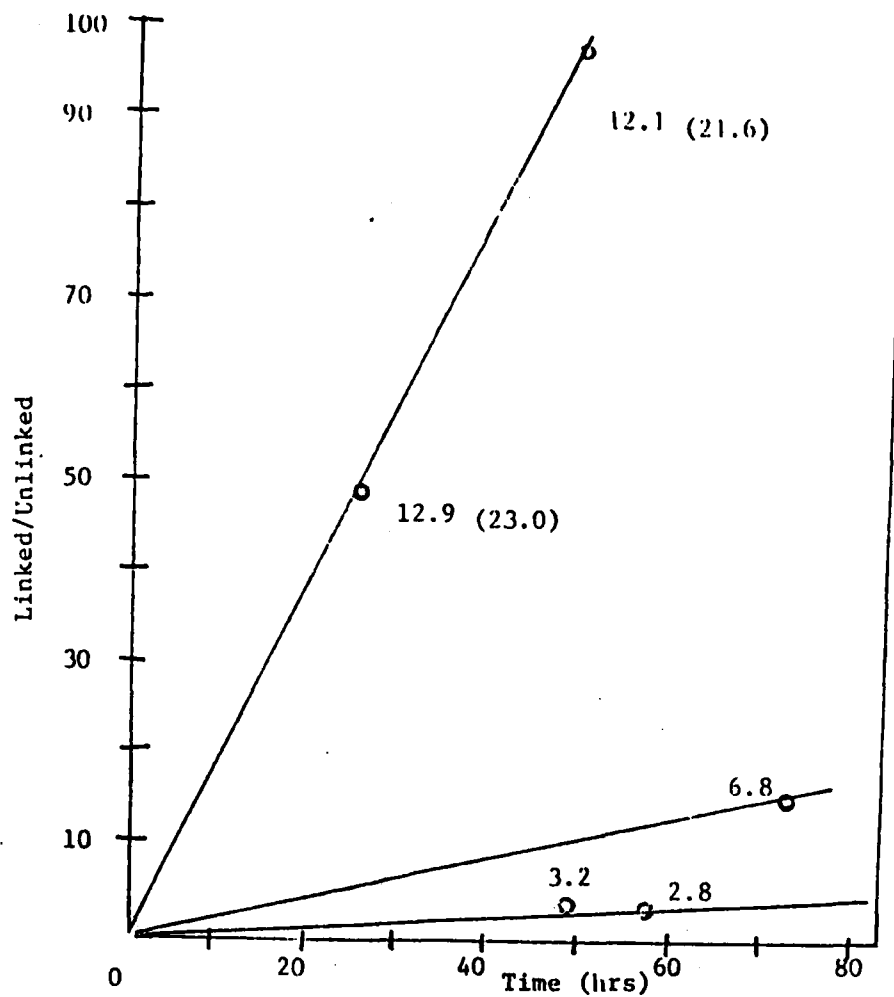


Figure 24. Linking Efficiency of Poly(butadienyl-lithium) Anions at 45-50°C for Various DVB/RLi Molar Ratios.

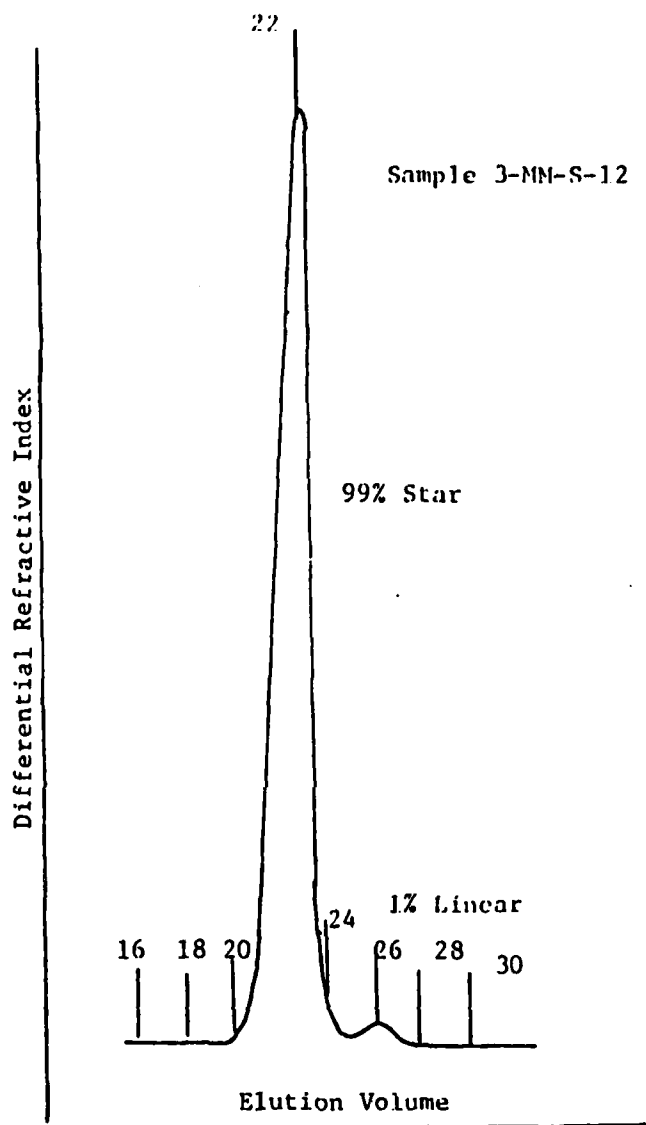


Figure 25. G.P.C. Trace for a Star-branched Poly(butadiene) Linked for 48 hrs. at 50°C with DVB/RLI= 12.1.

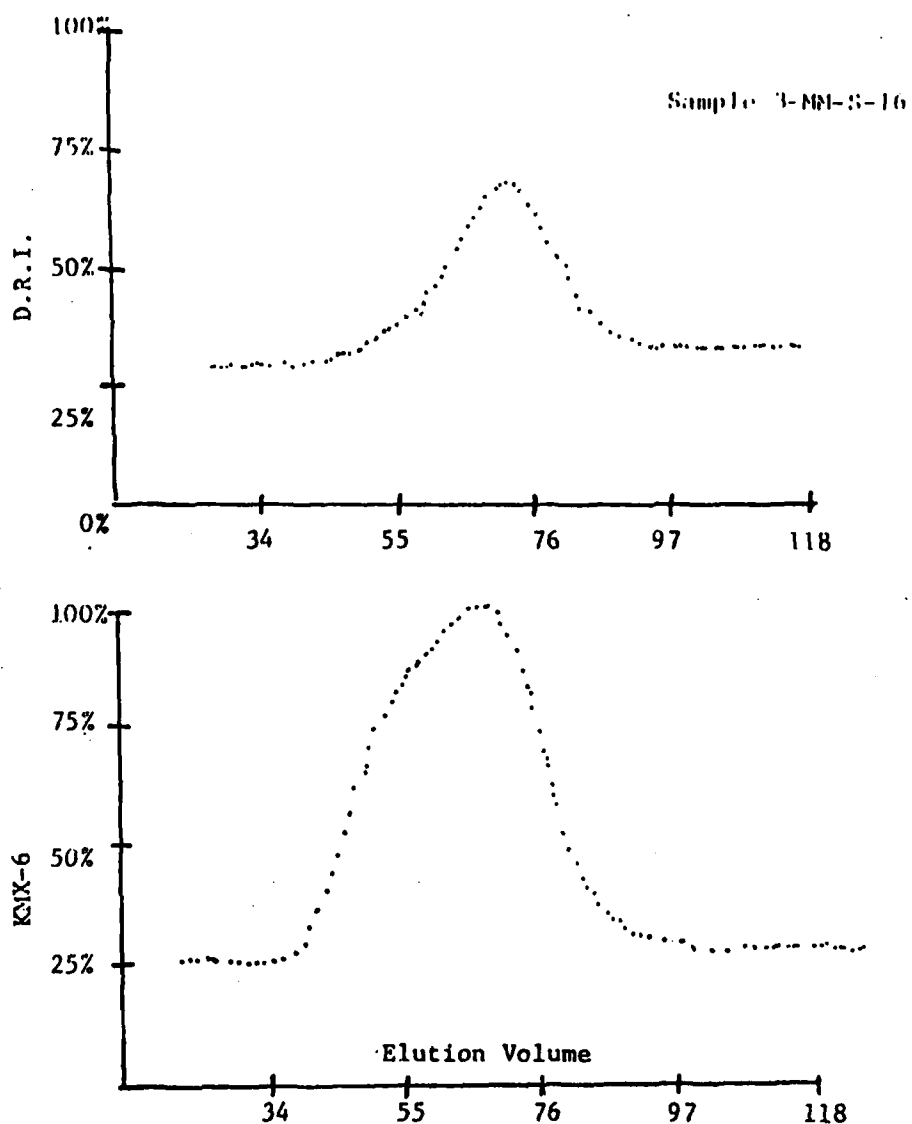


Figure 34. KMX-6/ DP G.P.C. Detector Response for Sample PI-S-16, a Star-branched Polymer Linked With DVB/RLi= 11.9.

(D.V.B. 25%)

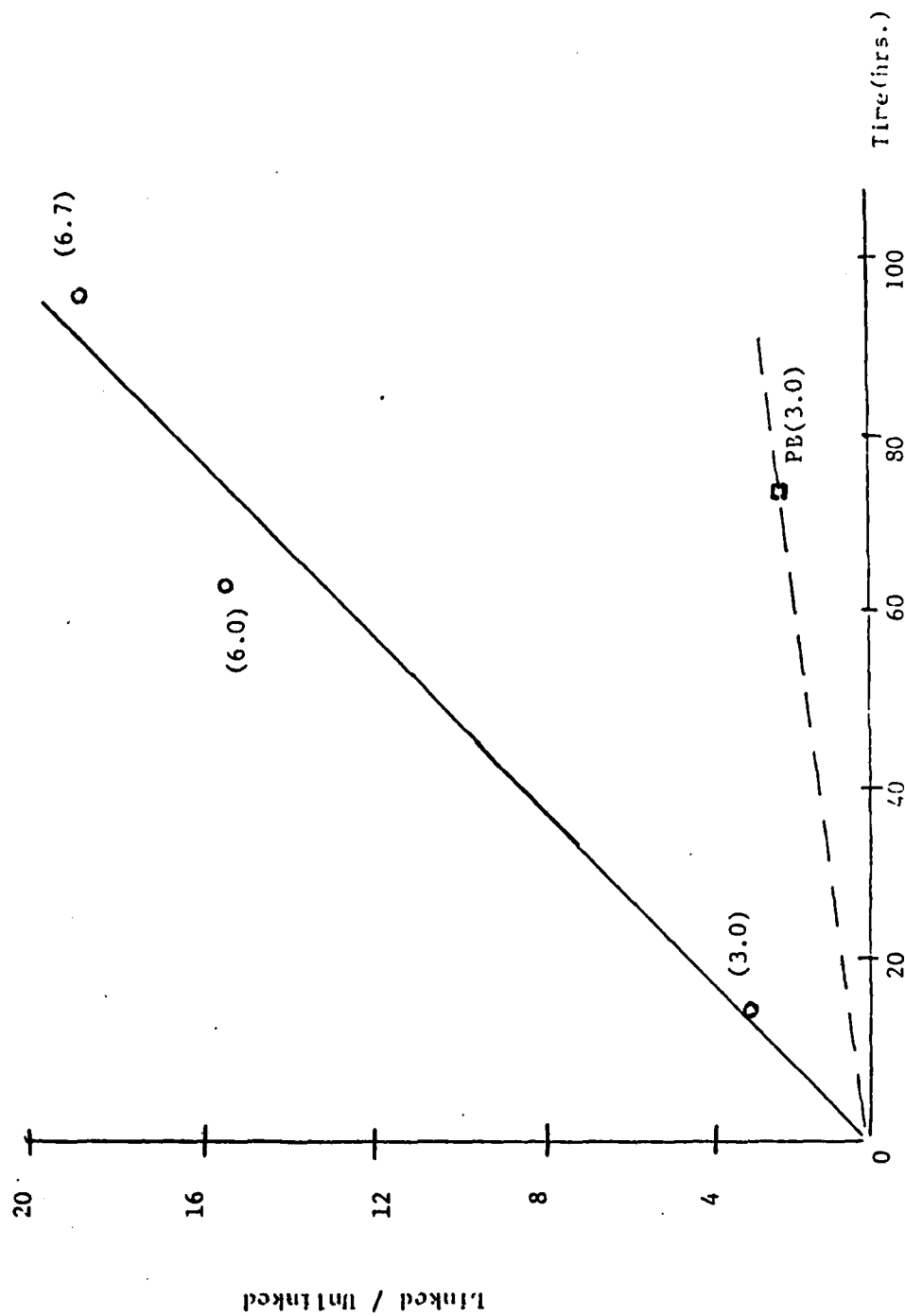


Figure 27. Linking Efficiency of Poly(isoprenyllithium) Anions at 25°C as a Function of Time and DVB/RLi Ratio.

Table I Data Summary for Poly(butadiene) Star Polymers

Sample	DVB/RLi ^a	\bar{N}_{arm}^b	%linear ^c	Reaction Time (hr.s)	T °C
2-MN-S-1	3.0	18	36D ^d	72	25
2-MN-S-5	5.9	--	29 ^e	24	45
2-MN-S-6	4.9	15	6	36	45
2-MN-S-7	3.2	23.4	21.9D	48	45
2-MN-S-8	2.8	18.4	25.7D	56	45
3-MN-S-12	12.1	16	1	48	50
3-MN-S-13	12.9	--	2	24	50
3-MN-S-15	6.8	23.8	5.9	72	50
4-MN-S-17a	4.0	--	33.1	6	25
4-MN-S-17b	4.0	--	13.8	24	25
4-MN-S-17c	4.0	--	4	152	25
4-MN-S-17d	4.0	--	2.4	163	25
4-MN-S-17e	4.0	--	1.7	200	25

(a.) DVB/RLi ratio has been corrected for 44% ethylvinylbenzene.

(b.) $\bar{N}_{arm} = \bar{M}_n(star)/\bar{M}_n(linear)$, (c.) wt. %linear from G.P.C.,

(d.) D represents linear coupled dimer., (e.) It is suspected some premature termination resulted for sample 2-MN-S-5.

Table II. Membrane Osmometry and G.P.C. Data Summary.

Sample	\bar{M}_n Linear	\bar{M}_n Star	Elution Volume ml Star	Elution Volume ml Linear
<u>Poly(butadiene)</u>				
2-NM-S-1	32,000	589,000	24.2 ^a	29.0
2-NM-S-6	64,000	959,000	22.7 ^a	27.0
2-NM-S-7	35,200	824,400	22.1	26.2
2-NM-S-8	34,800	614,000	22.1	26.0
3-NM-S-12	35,000	562,000	22.1	26.2
3-NM-S-15	35,000	833,700	22.0	26.2
<u>Poly(isoprene)</u>				
2-NM-S-2	27,550	211,500	24.5	28.3
2-NM-S-3	51,000	673,000	23.6	27.5
2-NM-S-4	55,700	562,000	23.5	27.6
2-NM-S-9	41,150	521,800	23.8	27.9
2-NM-S-10	39,800	389,000	24.0	28.0
3-NM-S-16	37,700	458,000	22.0 ^a	27.1

a.) G.P.C. data obtained with a different column arrangement.

Table II Chromatix Low Angle Laser Light Scattering G.P.C. Detector
Data Summary

Sample	Molecular Weight Light Scattering M_n (a) M_w (b)	Molecular Weight Membrane Osmometry	(M_w/M_n) l.s.	(M_w/M_n) o.p.	(c)
PI-S-16	422,641 563,200	458,000	1.33	1.23	21.2(11.9)
PI-S-16F	446,000 610,430	458,000	1.37	1.33	21.2(11.9)
PI-S-9	521,100 574,982	521,800	1.10	1.10	9.5(5.3)
PB-S-15	833,700 865,257	-----	1.04	-----	12.2(6.8)
PB-S-8	468,184 486,358	549,500	1.04	-----	5.0(2.8)

$(dn/dc) = 0.1407$ for Poly(isoprene) in THF at 25°C. (a) $M_n = \sum C_i / \sum C_i / M_i$ (b) $M_w = \sum C_i M_i / \sum C_i$

$(dn/dc) = 0.1398$ for Poly (butadiene) in THF at 25°C (c.) Values in parentheses are corrected for the presence of 44% ethylvinylbenzene.

Table ^{TJ} 1. Data Summary for Poly(isoprene) Star Polymers.

Sample	DVB/RLi ^a	\bar{N}_{arms}^b	Reaction Time(hrs.)	Temp. (°C)	%Linear ^c
2-MM-S-2	3.0	7.7	14	25	23%
2-MM-S-3	6.0	13.1	62	25	6%
2-MM-S-4	6.7	9.8	96	25	5%
2-MM-S-9	5.3	12.7	62	45	3%
2-MM-S-10	3.2	9.8	62	45	8.5%
3-MM-S-16	11.9	12.1	48	50	9.8%

(a.) DVB/RLi ratio has been corrected for 44% ethylvinylbenzene.

(b.) $\bar{N}_{\text{arm}} = \bar{N}_n(\text{star})/\bar{N}_n(\text{linear})$, (c.) Determined from G.P.C.

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III. Hydrogeneated Linear Block Copolymers of Butadiene and Isoprene: Effects of Variation of Composition and Sequence Architecture on Properties.

ABSTRACT

The effects of variation in molecular architecture and composition on bulk properties is reported for a series of well characterized hydrogenated block copolymers of butadiene (HB) and isoprene (HI) each having a total molecular weight of $\sim 200,000$ and a narrow distribution ($M_w/M_n < 1.17$). The polymers were synthesized from sequential anionic polymerization followed by hydrogenation, using p-toluenesulfonylhydrazide. The material properties of the homopolymeric HI and HB were also investigated. As expected, HI is rubbery at room temperature and HB is a tough semicrystalline plastic with properties similar to those of a low density polyethylene, LDPE.. The crystallinity, density and ΔH_f for all of the block copolymers were found to be linearly dependent on HB content indicating that little mixing exists between the semicrystalline regions and the rubbery blocks. Although the solution cast films of the block copolymers were spherulitic, the quenched films displayed no distinct structure on the supermolecular level indicating that the aggregation of the crystallites was more random in these films. The stress-strain properties of triblock copolymers with different block sequence, HBIB and HIBI, and a diblock copolymer, HBI, were similar in bulk behavior to each other in the high and the intermediate butadiene content (50-90%). This was related to the fact that the mechanical properties were determined predominantly by the behavior of the more continuous HB phase. For the lower butadiene compositions (7-29%), there was a major difference in the behavior of polymers with different block architecture. HBIB polymers were thermoplastic elastomers, whereas HIBI polymers behaved like an uncured

particulate filled rubber. This difference was related to the presence of permanent "entanglements" in HBIB polymers. The permanent entanglements which act as a physical crosslink are a consequence of the anchorage of the HB end blocks in the semicrystalline domains. No such arrangement is possible for either the HIBI or HBI polymers. The hysteresis behavior of HBIB polymers were strongly dependent on butadiene content, decreasing with lowering of the concentration of the semicrystalline HB. This dependence was related to the continuity of the crystalline microdomains. All the members of HIBI (and the HBI we considered) showed large hysteresis behavior. This large energy loss during cyclic deformation in these polymers was related to the absence of the permanent anchor points arising from end block crystallization.

INTRODUCTION

The ease in attaining a spectrum of properties through the modification of composition and block architecture has been a major factor in advancing the importance and use of block copolymers. The strong interest in block copolymers has produced a large number of publications in this field.¹⁻⁴ Although there are some reports on block copolymers containing a semicrystalline block such as poly(ethylene oxide)⁵ or even a semicrystalline polypeptides block such as poly(γ -benzyl-L-glutamate,^{4,6} the majority of the research has been focused on systems whose blocks are amorphous. The linear amorphous block copolymer of styrene-butadiene-styrene is produced commercially under the trade name of Kraton® and has been studied most extensively.¹⁻³ A hydrogenated version of this polymer, where the central block is believed to be of low crystallinity⁷, is also available (Kraton G-1650).

Significant modification in properties of polymers and block copolymers containing isoprene and/or butadiene have been reported following hydrogenation of these macromolecules.⁸⁻¹⁴ Although the initial motive for this modification of the double bond containing polymers was perhaps directed towards enhancement of the photolytic, oxidative, and thermal stability of these polymers, it was realized subsequently that polymers containing butadiene of low vinyl content produced better mechanical properties.⁹⁻¹⁴ This improvement can be attributed to the development of crystallinity in the polyethylene-like segments.⁸

Hydrogenation of the polyisoprene block results in the formation of the amorphous alternating copolymer of ethylene-propylene. The hydrogenated

polyisoprene (HI) block possesses a glass transition temperature below ambient temperature ($T_g \approx -42^\circ\text{C}$ by DSC, heating rate $10^\circ/\text{min}$) and is rubbery at room temperature. Exhaustive hydrogenation of the polybutadiene block of low 1,2 microstructure will transform this block to a polyethylene-like structure.⁸ Hydrogenation of 1,2 microstructure (present in the parent polymer in around 5-8 mole percent)* would result in formation of pendant ethyl groups. Therefore the resultant HB block is more similar in properties to low density polyethylene^{15,16} (but not exactly the same as LDPE¹⁷) than to high density polyethylene. The HB block is thus semi-crystalline but the crystallinity of this block in the quenched samples is lower than 35 percent. The low crystallinity of this exclusively hydrogenated HB polymer is due to the presence of pendant ethyl side chains.

Duck, et al., in their extensive studies of the hydrogenation reaction of polybutadiene showed that crystallinity of the product is dependent on the 1,4 content and the extent of hydrogenation.^{8,9} For samples containing 8 percent vinyl group, considerable crystallinity was developed after 50 percent hydrogenation. They also showed that the crystallinity was not dependent on the molecular weight of the parent polymers, but was linearly dependent on the extent of hydrogenation.⁸ This could indicate that when a long enough portion of the polymer is hydrogenated, it can aggregate itself into a crystal lattice. Thus segregation of crystallizable and amorphous segments, above 50 percent hydrogenation, permits formation of microcrystalline domains which

* 5-8 mole percent is obtained from IR of polybutadiene according to the procedure given in the text. This equivalent to 1.3-2.1 ethyl branches per 100 carbon atom. NMR analysis of the same HB obtained via courtesy of Prof. Mandelkern indicated the presence of ~2% ethyl branch units.

serve as physical crosslinks. Moreover, crystallinity which is detectable by X-ray diffraction is developed. At appropriate levels of hydrogenation and percent 1,2 content, these polymers behave as thermoplastic elastomers. Of course the use temperature must be well below T_m of the crystalline block and above T_g of the other block component.⁸

Falk reported the synthesis of triblock copolymers containing polyethylene-like end blocks and a rubbery central block by the catalytic hydrogenation of triblock copolymers of butadiene where end blocks were low in 1,2 microstructures but the central block was high in 1,2 microstructure¹⁰. He was also able to selectively hydrogenate butadiene blocks in copolymers of 1,4-butadiene-isoprene-1,4 butadiene.¹³ The point of importance is that hydrogenation of a polybutadiene segment which is rich in 1,4 microstructure will yield a semicrystalline polyethylene-like block whereas the block containing moderate to high 1,2 microstructure produces rubbery structure at ambient temperatures.

Hydrogenation of polybutadiene containing high 1,4 microstructure has also been employed for preparation of "polyethylene" of low polydispersity and various studies have been conducted on this polymer. In a series of papers, Graessley et al. discussed the preparation and the rheological behavior of linear and star-branched hydrogenated polybutadiene.^{15,16,18} Cowie et al. used a series of polybutadiene which had been hydrogenated to different extents in an attempt to determine the glass transition of amorphous polyethylene.¹⁹ The crystallization¹⁷ of HB has also recently been investigated. The rheology, dynamic mechanical behavior and the crystallization kinetics of HB were very similar to those of LDPE, but the elastic properties were different. In brief, this change was attributed to the difference in rigidity of the spherulites of HB from that of LDPE.

It is the objective of this work to investigate the effect of variation in block architecture (number and the order of the blocks) on the crystallinity level, morphology, the stress-strain and hysteresis behavior of this series of polymers. In addition, the composition ratio of the two block types are expected to play a crucial role in determining the bulk material properties of the block copolymers. This is related to the fact that the mechanical properties of block copolymers are typically influenced more substantially by the behavior of the continuous phase.^{1,21} The difference in properties of these polymers of varied architecture was most noticeable in the composition range where the semicrystalline domains are dispersed in the continuous rubbery matrix. Under this condition the HBIB polymer is a thermoplastic elastomer, but both HIBI and HBI behave somewhat as a particulate, partially filled uncross-linked rubbers. Similar behavior has been observed in block copolymers of styrene and butadiene.³

EXPERIMENTAL

Polymer Synthesis and Characterization

This topic has been extensively discussed in preceding papers.^{22a} However, we will briefly outline the preparative route. The block copolymers were synthesized via "living" anionic polymerization of butadiene and isoprene using sec-butyl lithium as initiator in hydrocarbon solvents under high vacuum. Under these conditions, the mode of addition of butadiene is predominantly 1,4, with between 5-8 mole percent of 1,2 structure.²³ Exhaustive hydrogenation of polymers were carried out in the presence of p-toluenesulfonylhydrazide^{18,24} in refluxing xylene. The relative block composition of the polymers were determined via NMR. The relative concentration of the various butadiene microstructures, (1,4 cis, 1,4 trans, and 1,2 vinyl), were determined from the infrared spectra of solid films cast on KCl.²⁵ The

1,2 microstructure content of all the polymers considered in this paper were between 5-8 as determined from the IR spectra. Number average and the weight average molecular weight of the polymers were obtained via osmotic pressure and HPLC. The molecular weight of all polymers is around 200,000 g/mole while the polydispersities were less than 1.17; thus, all of these polymers have a relatively narrow molecular weight distribution. A sample of low density polymer (LDPE) which was obtained from the Union Carbide Corporation (Dex 194) was used for comparison with our polymers. The number and the weight average molecular of this polymers, as obtained from GPC, were 13,900 and 77,500 g/mole, respectively.

The hydrogenated (H) block copolymers will be designated by giving the butadiene (B) or isoprene (I) block sequence followed by a number which represents the total weight percentage of butadiene in the polymer. For example HBIB-27 is a hydrogenated triblock copolymer of butadiene-isoprene-butadiene which contains 27% butadiene. Since the polymer is symmetric, the relative composition of each block is therefore 13.5% B - 73% I -13.5% B.

Sample Preparation

Samples for mechanical studies were made by compression molding the polymers at 150°C between Teflon sheets for 15 minutes followed by rapid quenching to room temperature in air. (These will be referred as PQ samples). Samples for morphology, SALS and SEM studies were prepared from toluene solutions. These films were cast on a Teflon sheet at 80°C from a 1% (by weight) solution in toluene. When the polymer films had solidified (after 5 hrs), they were stored in a vacuum oven at 80°C for two days to remove residual solvent. These samples will be designated by TOL (solution cast from toluene).

Crystallinity and Morphology

The X-ray diffraction patterns of the films were taken with a Phillips PW1720 table-top X-ray unit using a flat plate camera. The SALS H_v patterns were obtained using a Helium neon laser and the photographic technique developed by Stein.²⁶ An ISI Super III-A scanning electron microscope was employed for morphological investigations. Samples were coated with gold using a SPI sputter T.M., Model 13131. The density of the polymer samples was measured using a density gradient column constructed from ethanol and water. Glass beads with known density were used to calibrate the column. The thermal properties of the polymers were measured on a Perkin Elmer differential scanning calorimeter, Model 2C. The heating rate was 10°C per minute.

Mechanical Properties

The stress-strain and the hysteresis behavior of the polymers were measured on a Model 1122 Instron using dog-bone samples of 0.28 cm width and 1.0 cm effective length. Based on the initial length, the rate of extension as 100 percent per minute. The mechanical hysteresis of the samples, which is a measure of energy loss during cyclic deformation, was obtained from measurement of the area under loading and unloading curves using a plaimeter. The percentage hysteresis were calculated from the following relationship:

$$\% \text{ Hyst} = 100 (A_{\text{loading}} - A_{\text{unloading}}) / A_{\text{loading}}$$

where A is the area under the respective loading or unloading stress-strain curve.

RESULTS AND DISCUSSION

As already mentioned, the HB block is semicrystalline and its general behavior is similar to that of LDPE. The HI block on the other hand is amorphous and rubbery at ambient temperature. The material behavior of block copolymers containing HB and HI blocks will now be discussed in the following sections.

Crystallinity and Morphology

The block copolymers of essential completely hydrogenated HBIB, HIBI and HBI, in which the microstructure of butadiene is predominantly 1,4, are semicrystalline. Our measurements indicate that the extent of crystallinity is independent of the architecture of the block copolymer and is linearly dependent on the butadiene content. A comparison of the X-ray diffraction pattern of a homopolymer of HB is given in Figure 1 along with that from a triblock copolymer HBIB-50. The sharp diffraction rings are clearly indicative of the presence of crystallites in both polymers. Block copolymers containing as low as 8% butadiene have shown basically the same type of diffraction patterns, but with a much lower intensity because of lower concentration of butadiene. This indicates that aggregation of crystallizable segments and formation of crystalline domains is not significantly affected much by the surrounding noncrystallizable HI block.

Quantitative measurements of the crystallinity content of the block copolymers were made from the determination of the heat of fusion and from the density of the polymer.

The DSC thermograms of several triblock copolymer and homopolymer HB are compared to that of a low density polyethylene in Figure 2. The thermograms are those of the first run on quenched samples. Their behavior is similar

except that the temperature of the maximum in the DSC peak T_m for LDPE (110°C) is higher than that of HB (102°C). The depression of the melting point brought about by the presence of 5 to 8 mole percent of the side chain (equivalent to 1.3 to 2.1 ethyl per 100 carbon) far exceeds the theoretical value based on Flory's work.^{27a} Polyethylene containing methyl, ethyl and n-propyl groups have also shown higher depression of melting point than the theoretical value and thus the behavior of our system is not unique.^{27a,b} What is surprising, however, is that the depression of the melting point brought about by the presence of 1.3 to 2.1 ethyl branches per 100 carbon in our system ($\Delta T = 36^\circ\text{C}$ with respect to T_m of HDPE) is still much higher than that produced by the same amount of ethyl or even n-propyl branches ($\Delta T = 22^\circ\text{C}$).^{27a} At this point we do not have the exact reason for the behavior of our system, but it is possible that the higher depression of the melting point is caused a very small amount of remaining unsaturation and/or the presence of some p-toluene sulfonyl adduct produced during the hydrogenation of the double bonds. We have recently reported that the addition of a phenolic antioxidant such as Irganox 1010 effectively decreases the minor, but the detectable side reaction.^{22b} We are currently investigating the effect of reducing the sulfonyl adduct concentration on T_m of the HB polymers. The preliminary results indicate that a decrease in concentration of the bulky adduct increases the T_m of the polymer, as expected. Other workers have also reported a lower T_m for HB polymers^{17,20} and they also postulated that the depression of the melting temperature, as compared to HDPE, is due to presence of ethyl branches and some remaining unsaturation in the main chain.¹⁷ Lowering of T_m with an increase in the number of ethyl side chains has been observed in copolymers of ethylene-butene.^{27c} Although the melting temperature of HB has been reported to be inversely related to molecular

weight²⁰ and hence on chain length, our block copolymers do not show such a dependence on HB sequence length. The "peak" melting temperature of all of the block copolymers, regardless of chain architecture or butadiene composition, are in the vicinity of $102 \pm 2^\circ\text{C}$ for the quenched samples. The reader may recall that for a given total molecular weight, an increase in butadiene content is followed by an increase of butadiene block chain length. Thus, neither the architecture nor the butadiene block chain length (at least in the ranges that we have studied) affects the melting behavior of the polymer. This is contrary to the finding of O'Malley, et al. who studied the effect of the changes of composition of tri and diblock copolymers of styrene ethylene oxide block copolymers.^{27d} They attributed the decrease of T_m of the crystalline polyethylene oxide block with the increase of styrene content to the decrease of the perfection of the crystalline PEO lamella. In light of this result, the independence of T_m on composition in our own systems could be rationalized in the following way. The crystallites of HB are generally embedded within the amorphous HB phase and thus are not affected by the rubbery HI block because the percent crystallinity of HB is low. Thus the environment experienced by the HB crystallites is the same, unlike the previous work^{27d} and therefore their perfection (and hence T_m) is not influenced by the composition variation of HI.

Regarding crystallinity contents, the heat of fusion ΔH_f , obtained from the area under the DSC melting curve, (and subsequently the percentage crystallinity calculated from ΔH_f) is found to be linearly dependent on butadiene content, and independent of the polymer architecture. This is shown in Figure 3. Also, the density of the block copolymers was found to be linearly dependent on butadiene content (see Figure 4). The linear additivity of density (specific volume) has been observed by other workers for

incompatible block copolymers of styrene and butadiene indicating that that very little change in density from that of pure components has occurred on forming the block copolymers.²⁸ While somewhat plausible, other workers have utilized the small positive deviation from the linear additivity law to estimate the thickness of the boundary in SB block copolymers.²⁸

In Figure 4, the density of a random hydrogenated copolymer of butadiene-isoprene containing 50% butadiene is also given. The X-ray diffraction pattern and the DSC thermogram of this polymer indicates that it is totally amorphous. Extrapolation from the density of HI to the density of this random HBI-50 to the axis corresponding to 100% hydrogenated butadiene would give the density of amorphous HB (or that of amorphous "polyethylene"). The value of the density for amorphous polyethylene obtained in this way is about 0.869 g/cm³ as compared to the value of 0.855 g/cm³ obtained from the extrapolation of molten PE.²⁹ In our calculation of the percentage of crystallinity from density measurements, we have used this value of 0.869 g/cm³ for the density of amorphous PE, (rather than the literature value of 0.855 g/cm³) 0.862 g/cm³ for the density of hydrogenated isoprene (amorphous), and 1.00 g/cm³ for the density of crystalline PE.^{30a} The value of crystallinity obtained using the above values is nearly identical to that found from ΔH_f . This value is at least 12% lower than that found using the relationship of Chiang and Flory where the density of the amorphous and crystalline PE are taken at 0.8518 and 0.9995 g/cm³ respectively at 25°C.^{30b} The percent crystallinity was also obtained from the areas of the endothermic peaks in DSC graphs using a ΔH_f value of 69 cal/g for completely crystalline polyethylene.³¹ A comparison of crystallinity values obtained from density to those from ΔH_f is made in Figure 5. The correspondence of the density from both methods is excellent. It is noteworthy that the behavior of LDPE also falls in this range, even

though the crystallinity of this sample is much higher. It is of interest to point out that Hser and Carr have reported percentage crystallinity of a series of HB of different molecular weight using the X-ray diffraction method. The density of all of their samples were $\sim 0.915 \text{ g/cm}^3$ and for samples in the molecular weight range 60,700 to 340,000 the ΔH_f were 21.7 cal/g to 17.4 cal/g respectively. These ΔH_f values correspond to a percent crystallinity varying from 31.4% to 25.3% whereas the respective percent crystallinity values from the X-ray method were 43% and 46%. That is, there is little correlation in their crystallinity values obtained from the ΔH_f and X-ray methods used in their work. While we do not attempt to explain their discrepancy, it stands on contrast to our own data. The important point to be made at this time is that an increase in crystallinity in our series of block polymers is only dependent on the butadiene content and bears no relationship to the block architecture.

The accumulated data from X-ray, ΔH_f and density measurements thus far indicate that there is good separation of the crystallizable HB block from that of amorphous HI block, regardless of molecular architecture. We as yet have no direct evidence to determine what is the specific morphological nature of the crystalline structure. Specifically, whether they are composed of fringe micelle or folded chain structures. Dimarzio et al. have carried out calculations of lamella thickness in diblock copolymers, one of whose components is crystalline, have reached the conclusion that chain folding is a stable form in these block copolymers.³² This is contrary to homopolymers where chain chain folding is metastable and annealing reduces chainfolding.³³ In order to gain some insight into possible arrangement of the crystalline domains on a high order level i.e., superstructure, we have applied the SALS technique. The H_v patterns for solution cast films of HB and a series of HBIB

polymers are shown in Figure 6. Both the HIBI and HBI polymers produce the same kind of patterns and are not shown here. Polymers with high and intermediate butadiene content clearly display the typical cloverleaf H_V pattern which is associated with the spherulitic structure.³⁴ In this composition range, the size of the spherulites as calculated from the angle of the maximum intensity in the H_V four-leaf clover scattering patterns, range from 0.5 to 3.0 μm . One also observes a deterioration of the spherulitic perfection with an increase in HI content, and indeed sample HBIB-7 no longer displays cloverleaf patterns, but rather a more rod-like or sheaf type patterns. SEM micrographs of two members of these polymers (HB and HBIB-50) are shown in Figure 7. One can directly observe the surface spherulitic structure of the HB homopolymer as well as in that of the copolymer HBIB-50. The H_V patterns shown in Figure 6 display an important trend. The best formed spherulitic structure is that of homopolymer HB. When the concentration of butadiene decreases in the series of the HBIB copolymer the perfection of the spherulites is also decreased. Indeed in the polymer HBIB-7, which contains only 7% butadiene, one can no longer see the H_V scattering pattern of well developed spherulites. It is to be noted that the formation of the spherulitic structure is strongly dependent on the method of the film preparation. The well developed spherulitic structure shown in Figure 6, HB or HBIB-86 for example, were produced when the films were cast from solution (Tol). By contrast, press-quenched sample (PQ) did not show well developed spherulitic structure. Even the HB homopolymer produced a very ill defined spherulitic pattern when the film was prepared by quenching the pressed film. Mandelkern et al. have studied supermolecular structure of linear polyethylene fractions and reported that high molecular weight fractions ($3 - 8 \times 10^6$) do not form well developed spherulites if they are crystallized rapidly.³⁵ These

polymers can, however, produce spherulitic structure if they are crystallized from highly swollen solutions.³⁶

It should be reemphasized that although our block copolymers do not display spherulitic structure when they are press-quenched, they are nevertheless crystalline. This indicates that under this mode of film preparation, aggregation into well developed superstructure does not occur.

Stress-Strain Properties

A comparison of the stress-strain properties of the press quenched triblock HBIB copolymers to those of the homopolymers HB and HI of the same molecular weight (~200,000) are made in Figure 8. The stress-strain properties of the inverted triblock copolymers HIBI are given in Figure 9. As might be expected, the stress-strain properties of HB are very similar to that of low density polyethylene. Perhaps linear low density polyethylene (LLDPE) would be an even better model. The major difference that we have observed is that the initial modulus of HB is lower than that of LDPE (75 vs. 170 MPa respectively) and there is also a lower stress displayed in the region where plastic deformation begins which is likely associated with yielding phenomenon involving crystallite reorientation. Both of these differences are at least partially accountable by the lower crystallinity of the press-quenched samples of HB relative to that of low density polyethylene (the crystallinities are approximately 30% and 40% respectively, see Figure 5). Onogi et al., however, have reported that the materials properties of HB are different from that of LDPE, the most remarkable difference is their higher elastic recovery.¹⁷ They attribute this difference to a "looser" structure of spherulites of HB which allows crystallites to orient in a reversible manner. We have not observed significant differences in the nature of the stress-strain behavior of HB polymers relative to those of LDPE. Indeed, when a sample of HB was prepared

by solution casting from toluene, the crystallinity of this film was very close to that of a quenched sample of LDPE. The stress-strain plot of this solution cast film closely resembled that of quenched LDPE, indicating, as mentioned before, the earlier difference is most likely principally due to the difference in the crystallinity level in contrast to molecular weight distribution discrepancies, etc. One should comment that the ultimate tensile properties of the HB systems are excellent.

The mechanical properties of HBIB block copolymers are significantly affected by the increase in the proportions of the central rubbery HI block. HBIB-86 (14% isoprene) shows a lower modulus; some yielding behavior is still present but elongation to break is significantly improved. A further increase in the rubbery HI content (eg. from 14 to 82%) produces a modulus which is sharply decreased, but the elongation to break is again increased. HBIB-70 and HBIB-50 are very tough plastics; the former has even a higher stress to break than the initial HB. On the other hand, the behavior of HBIB-27 is typical of a thermoplastic elastomer. HBIB-18 also has elastomeric behavior but it fails earlier than HBIB-27 indicating that the three dimensional network of physical crosslinks (crystallites) is less well developed. The behavior of HBIB-7 is somewhat like a particulate filled and uncrosslinked rubber of low filler content. The last member of this series, the homopolymer HI (or HBIB-0), is and behaves as an uncured rubber. It does not show any strain hardening indicating that, as expected, at the level of strain experienced by the sample (~240%) no strain-induced crystallization occurs.

The general stress-strain behavior of our HBIB series has some similarity to those of the SBS block copolymers.³ However, there are two prime differences between these two systems. Styrene is a brittle glass at room temperature, but HB is a semicrystalline plastic above its T_g and therefore is rather ductile. Therefore, a block copolymer of SBS containing as much as 20%

butadiene is still brittle and often broken at very low elongation. By contrast, HBIB-86 or even HB itself can be extended to above 400% elongation before failure occurs. The other difference is that the block copolymers of SBS may show considerable amounts of drawing (necking) in the concentration range of 39% to 65% styrene, whereas none of the members of HBIB display this behavior.

The stress-strain properties of the inverted triblock copolymers HIBI are shown in Figure 9. Analogous measurement on the diblock copolymer HBI-50 are not shown but were almost identical to that of HIBI-49.

As expected, an increase in isoprene content from the homopolymer HB polymer to the HIBI block copolymers and finally to the homopolymer HI greatly influences the mechanical properties. An increase in the rubbery HI content is again followed by a decrease in modulus. In the range of 23% to 49% butadiene, the polymers show higher extension to break than for the HB. They can be viewed as tough plastics and require a larger input of energy (higher area under the stress-strain curve) to break. The next member of the series, HIBI-29, shows a great deal of extensibility, but it is extremely weak. A further increase in isoprene concentration results in polymers which not only are weak but also break at low extensions (HIBI-19 and HIBI-10). Now that the effects of variation of composition on the mechanical properties of each member of the two series has been examined, the influence of architecture alone on properties can be considered. A comparison of modulus of polymers of various architecture and different compositions are made in Figures 10A-C and Figure 11. As in the case of Figure 10A, an increase in HB content, i.e., a rise in the concentration of the semicrystalline blocks, is always followed by a rise in the modulus of the polymers. This type of behavior of block copolymer has been expressed in terms of composite theories and the knowledge

of the modulus of the component blocks (HI and HB). To do so, however, one has to know the geometry of the microdomains in the system considered. Calculation of the modulus of block copolymers using the modified composite theories developed by Nielsen^{37,39} and Lewis³⁸ have been reported on SBS triblock copolymers^{40,2} and need not be repeated here.

An interesting observation derived from Figure 10A is that modulus of the triblock copolymer HBIB is always considerably higher than that of the inverted block copolymer HIBI. This difference in modulus is likely due to the presence of more permanent entanglements in HBIB copolymers since these end-blocks can be partially tied down in the semi-crystalline domains, as shown schematically in Figure 12. Of course, it is realized that amorphous regions in HIBI do form entanglements, but since end blocks are not mechanically anchored these entanglements can be lost when the sample is deformed. The ultimate properties, that is the elongation and stress at break for copolymers with various architectures and compositions, are given in Figures 10B and 10C respectively.

The elongation at break ϵ_B goes through a maximum for the block copolymer when the composition is varied from pure HI to that of HB as shown in Figure 10B. The maximum is achieved around 30% butadiene content. Since the ultimate properties are often controlled by crack initiation and crack propagation steps^{41,42} the improvement in ϵ_B here suggests that this catastrophic failure has been reduced by some mechanism. One of these principal mechanisms is believed to be the termination or slowing down of the crack front at the boundary between the crystalline and noncrystalline regions. Thus in the composition range of 30% to 40% butadiene content, the morphology of all of the polymers, HBIB, HIBI and HBI, is perhaps in an optimum condition for arresting catastrophic failure. Therefore all of these polymers have high extension in

this concentration range. Above this concentration range ϵ_B is again decreased, but now there is a considerable difference in behavior of HBIB from that of HIBI polymers. In the 10% to 20% butadiene range HIBI polymers fail at lower elongation than HBIB polymers and this behavior is related to the morphological structure of the polymers as discussed shortly. The stress to break σ_B does not seem to go through a significant maximum, but rather there is a considerable increase in σ_B with an increase in butadiene from the low value of HI. The behavior of the polymers in regard to ultimate stress falls into two categories. In the low to intermediate concentration range of butadiene (from 10% to 40% B) the behavior of the HBIB polymers is quite different from that of the inverted HIBI copolymers and is most pronounced in the 20-29% range. In the high concentration range (40% to 100% B), and σ_B for HBIB and HIBI is much closer. A comparison of the stress-strain properties for HBIB and HIBI polymers, in this concentration range, is made in Figure 11.

The HBIB-27 polymer behaves like a thermoplastic elastomer, whereas HIBI-29 behaves somewhat like a particulate-filled uncured elastomer. These differences are clearly related to the morphology and structure of these polymers. To describe the behavior of these polymers of various architecture containing different levels of semicrystalline HB block, a model, but oversimplified schematic drawing of these polymers was made at the two extreme ranges in concentration.⁺ Thus, in polymers where the relative concentration of butadiene is high (Figure 12), the continuous phase is the semicrystalline

⁺ These drawings are not meant to infer that no superstructure or chain folding may exist but only to depict the general differences in the continuity of the two components as well as the nature of the localized end block.

HB (or the poly-ethylene like structure). The mechanical properties of the polymer is controlled primarily by this continuous dominant phase. The rubber HI domains are dispersed within this semicrystalline phase. There is no major difference between HBIB, HIBI or HBI block copolymers because the properties are determined by the continuous semicrystalline structure. The behavior of this system is somewhat similar to that of rubber modified polystyrene.¹ The main function of the dispersed rubbery phase is to lower the modulus and to allow higher extensibility by terminating or reducing crack propagation. A schematic drawing for the intermediate concentration of butadiene is not shown but the behavior is similar since under this condition (of course, depending on the film processing condition) both phases are continuous. But the behavior of the polymer is again controlled by the dominant semicrystalline phase.

The schematic drawing of morphology of the block copolymers in the low butadiene range is also given in Figure 12. In this concentration range of the behavior of the HBIB polymers is very different from that of HIBI or HBI. The continuous phase in this case is the rubber HI segments and the semicrystalline domains are dispersed throughout the sample. The semicrystalline domains in the case of HBIB not only act as a filler, but also tie down the end blocks of the polymer producing physical crosslinks. The entanglements in the HI blocks can no longer be opened by complete slippage of the chain, and are therefore of a more permanent nature. The behavior of HBIB polymers under this condition is that of a thermoplastic elastomer. The HIBI or HBI polymer cannot form this kind of physical cross-links, the HB block which has formed the semi-crystalline domain can only act as a filler and therefore these polymers behave like an uncured rubber. This type of behavior has also been observed for SBS block copolymers.³

Hysteresis Behavior

The hysteresis behavior of the HBIB triblock copolymers are given in Figure 13A and of that of the inverted HIBI block copolymer is given in Figure 13B. The difference in the behavior of these two series of block copolymers is tremendous. The origin of these differences are again directly related to the morphology and the architecture of the polymers. The hysteresis behavior of HBIB is strongly dependent of the composition of polymer. The first member of this series is the homopolymer HB which contains the highest (100%) concentration of the semicrystalline segment and therefore exhibits the highest hysteresis. That is, during each cyclic loading and unloading, a considerable amount of energy is lost as heat. Moreover, irreversible rearrangement of the crystalline domains occurs during this plastic deformation.

Introduction of the central rubbery HI block decreases the continuity of the semicrystalline domains and results in a successive decrease in hysteresis behavior. Similar behavior has been observed in segmented polyurethanes when the hard segment content has been varied.⁴³ Thus, increase in HI block content (or a decrease in the concentration of the semicrystalline HB) is always followed by a large decrease in the hysteresis behavior. The lowest hysteresis is observed for HBIB-7 which contains the lowest butadiene content, but this sample is not very extensible and fails early because, as mentioned before, there are not enough crystalline domains to form a three dimensional network of physical crosslinks. HBIB-18 and HBIB-27 which are both thermoplastic elastomers, show considerable plasticity but low hysteresis behavior. The hysteresis behavior of the above two elastomers is much lower than that of the conventional segmented poly(urea-urethanes).⁴⁴ An increase in the butadiene content of the other members of the HBIB series results in the crystalline HB domains developing more continuity. This alteration in morphology

leads to a higher hysteresis. Further support of the above argument extends from the recent work of Sequela and Prod'homme who investigated the properties of SIS and SBS block copolymers.⁴⁵ They have shown that the best hysteresis behavior is obtained for samples in which the hard styrene block has formed microdomains which are well isolated from each other.⁴⁵ This was actually demonstrated much earlier by one of the authors.⁴⁷ The mechanical behavior of such a system is similar to that of unfilled crosslinked rubber. If, however, the samples were made such that there was connectivity between the hard blocks, the mechanical properties deviated from that of cross-linked rubber. Similar observation have been made with respect to the hysteresis behavior in segmented urethanes as a function of composition and domain morphology.

The hysteresis behavior of the HIBI series is shown in Figure 12B. All of the samples have much higher hysteresis than the corresponding member (with respect to composition) of the HBIB series. Although there is a noticeable decrease in the percent hysteresis with an increase in rubbery HI content, the hysteresis does not fall below 55% at high extensions.

The hysteresis behavior of the diblock copolymer HBI-50 is not shown but is very similar to that of HIBI-49. In summary then, the difference in hysteresis behavior of the HBIB series to that of HIBI and HBI is related to the ability of the members of the first series to form permanent entanglements, by entrapment of the end blocks in the semicrystalline domains, whereas no such arrangement is possible for neither HIBI nor HBI series. The permanent entanglement serves as a physical crosslink which promotes recovery of the polymer after the deforming stress has been removed. At the same time, there is much lower energy lost as heat.

Crystallization Kinetics

Changes in the composition of the block copolymers affects their rate of crystallization. To indicate this, a plot of the time, t_{xta} , between the onset of crystallization to the time of maximum crystallization rate, i.e., the maximum in the C_p versus time curve at a fixed temperature is plotted against the degree of supercooling in Figure 14A. The supercooling is defined as the melting temperature minus the crystallization temperature. In this study, we have taken the temperature of the exothermic maximum of the DSC curve as the melting temperature. In the above plot, the polymer with a faster rate of crystallization will have a curve which is shifted closer to the origin. The rate of crystallization of the homopolymer HB and block copolymers of HBIB are compared to that of our LDPE sample in Figure 14A. It is noted that the LDPE crystallizes faster than the HB and the rate of crystallization of the block copolymers is lower than that of the homopolymer HB and decreases with an increase in HI content. This plot can also be utilized in two different manners. At any given supercooling, the sample with a faster crystallization rate will require a lower value of t_{xta} . The other way of describing the relative rate of crystallization is to determine the supercooling required for a given t_{xta} ; in this case samples with a faster rate will require a lower supercooling. Figure 14B is based on using this latter method of comparison. In this plot we have arbitrarily chosen the time window of t_{xta} to equal 50 seconds. Observe that the LDPE requires a 9 degree supercooling and has a faster relative crystallization rate than HB which requires a 10 degree supercooling. HBIB-50, in turn, requires a higher supercooling than HB. It is noted that the rate at this butadiene content also seems to be dependent on the molecular weight. The sample with a higher total molecular weight crystallizes more slowly as might be expected.

However, with the limited samples studied, this point should be viewed only as speculation.

The slowest rate of crystallization is observed for HBIB-27, whose molecular weight is around 190,000. Thus, the general trend indicates that the increase in rubbery block content (and therefore a decrease in crystallizable block content) results in a slower rate of crystallization. The melting temperature on the other hand is $\sim 102 \pm 2^\circ\text{C}$ for all of these polymers and does not depend on the block composition and the architecture. This latter data supports the earlier suggestion that there is not much mixing in the boundary between the two block types. Thus, if the decrease in the crystallization rate of the block copolymers is not likely caused by an increase in the relative concentration of a mixed phase, the question would be what is causing the difference in the values of t_{xtal} with a change in composition? A plausible, but highly speculative answer to this question may be the lowering of the rate of nucleation of the crystalline domains caused by their separation from each other due to the rubber HI phase. This situation has some similarity to the crystallization kinetics behavior of polyethylene droplets suspended in oil.⁴⁶ In our case, the amorphous HI phase plays the role of the oil. Even if there might be no change in the rate of primary nucleation and crystal growth, the bulk crystallization of polymer droplets in oil will be reduced. The reduction of the crystallization of the bulk of the polymer is due to the physical separation of the droplets (or HB domains in our case) because the propagation of crystallization will be restricted to the droplet in which the crystallization nucleus is initiated. The reduction of mass crystallization rate thus will be related to the lack of mechanism of transfer of crystallization from one domain to the neighboring regions. Further detailed crystallization and morphological studies will hopefully shed light on this phenomenon.

CONCLUSIONS

The mechanical properties of block copolymers composed of rubber HI segments and the semicrystalline HB chains are dependent both on the composition of the polymers and the architecture of the blocks. The density, ΔH_f , crystallinity and the morphology of the block copolymers, on the other hand, are only primarily dependent on butadiene content and show little dependence on architecture. This is tentatively indicative of the fact that there is a very good phase separation between the semicrystalline regions of the HB and rubber blocks, i.e., little or no mixing between them. Although the solution cast films show spherulitic morphology, the quenched films do not show distinct structures indicating that the arrangement of the crystallites in the supermolecular level is not well organized.

At high and intermediate concentrations of the HB block, where the semicrystalline block form the continuous or one of the continuous phase, the mechanical properties of the samples are controlled by this phase. At these compositions, the stress-strain properties are not much different, although there is a difference in modulus behavior between members of varied architecture. The hysteresis behavior is nevertheless significantly varied indicating that the permanent end block entanglements produced in the HBIB series play an important part in retracting the sample once the extension load is removed. The difference in mechanical properties between polymers of different architecture is most apparent when the HB content is low. At this composition, where the rubbery HI has formed the continuous phase and the semicrystalline blocks are dispersed in more discrete or isolated domains, the behavior of HBIB becomes of that of a thermoplastic elastomers. The HIBI and HBI polymers, on the other hand, cannot behave as crosslinked elastomers because they are not capable of forming permanent endblock anchorage. The stress-strain

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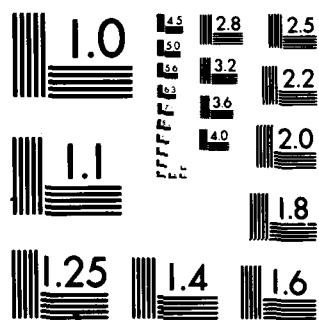
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MICROCOPY RESOLUTION TEST CHART
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properties of HIBI and HBI are similar to that of modified particulate filled uncured rubber. These polymers, however, have high extensibility, probably due to crack termination at the interphase. But contrary to HBIB polymers, they do not show any strain hardening and are very weak materials. The hysteresis behavior of HIBI and HBI polymers is also very different from that of the HBIB polymer. The former polymers show tremendously higher energy loss during cyclic deformations, and these differences are again interpreted as being related to the ability to form permanent entanglements.

ACKNOWLEDGEMENT

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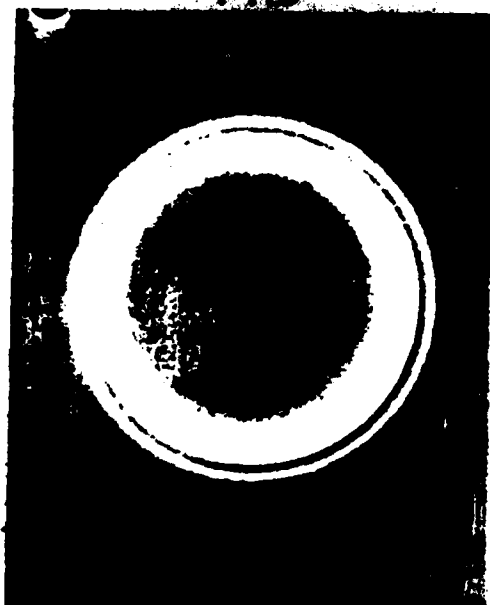
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FIGURE CAPTIONS

- FIGURE 1 X-ray diffraction patterns of the semicrystalline homopolymer (HB) and a block copolymer (HBIB-50).
- FIGURE 2 Comparison of the DSC thermograms of the homopolymer HB and various block copolymers to that of the LDPE. The weight of each polymer sample is indicated in the parentheses; the range of the instrument is 2 mcal/sec for all the runs.
- FIGURE 3 The linear dependence of ΔH_f on butadiene content in the various block copolymers.
- FIGURE 4 The linear dependence of density on butadiene content in the various block copolymers. The density of amorphous HB (polyethylene) is estimated from the extrapolation of the density of HI through that of the random copolymer HBI-50 to axis where butadiene content is 100%.
- FIGURE 5 A comparison of % crystallinity obtained from density to that obtained from ΔH_f for the various block copolymers.
- FIGURE 6 SALS, H_v light scattering patterns of homopolymer HB and the triblock copolymers HBIB of different compositions (indicated in the top left corner). The method of film preparation of T.C., cast from toluene (TOL) or press-quenched (PQ), is indicated on the top of the pictures. The exposure time (in fractions of a second) is indicated in the right hand corner of each picture.
- FIGURE 7 SEM of the surface of films cast from toluene for HB and HBIB-50.
- FIGURE 8 Comparison of the stress-strain properties of the press-quenched films of HBIB to those from the homopolymers HB and HI. The composition of each polymer is denoted by giving the butadiene content next to the graph.
- FIGURE 9 Comparison of stress-strain properties of the press-quenched films of HIBI block copolymers to those of homopolymer HB. The butadiene content is indicated next to each graph.
- FIGURE 10A The dependence of Young's modulus on butadiene content for the various copolymer architectures.
- FIGURE 10B The dependence of strain to break on the butadiene content for the various copolymer architectures.
- FIGURE 10C The dependence of the ultimate stress on the butadiene content for the various copolymers architectures.

- FIGURE 11 A comparison of the stress-strain properties of the thermoplastic elastomer HBIB-27 to that of the inverted block copolymer HIBI-29.
- FIGURE 12 Oversimplified schematic representation of the morphology of HBIB and HIBI block copolymers in the low and high butadiene concentration ranges. Formation of "physical crosslinks" by the anchorage of the chain ends in the semicrystalline domains and production of the "permanent" entanglements is shown in the HBIB block copolymers. No such arrangement exists for the inverted polymer HIBI. No attempt has been made to show possible chain folding, or superstructure development of their absence.
- FIGURE 13A The hysteresis behavior of the HBIB polymers.
- FIGURE 13B The hysteresis behavior of the HIBI polymers
- FIGURE 14A A comparison of the rate of crystallization for homopolymer HB and some of the triblock copolymers HBIB contrasted to that of LDPE. The molecular weight of the homo and the block copolymers ($\times 10^{-3}$) are indicated in the parentheses.
- FIGURE 14B A comparison of the supercooling to produce the onset of crystallization at 50 sec for LDPE, the homopolymer HB and some of the triblock copolymers of various compositions.

HB



HBIB-50

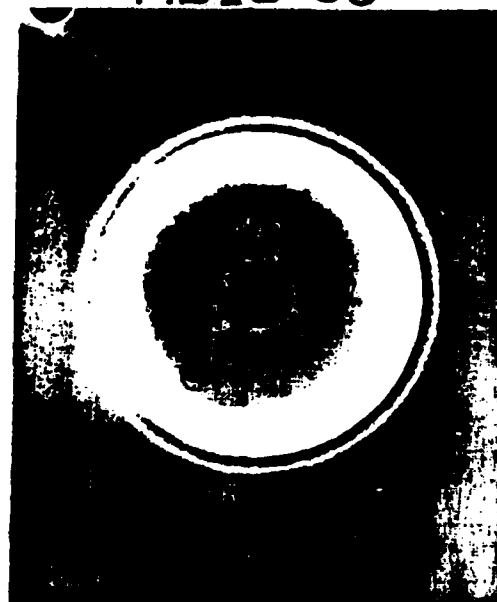


Fig. 1

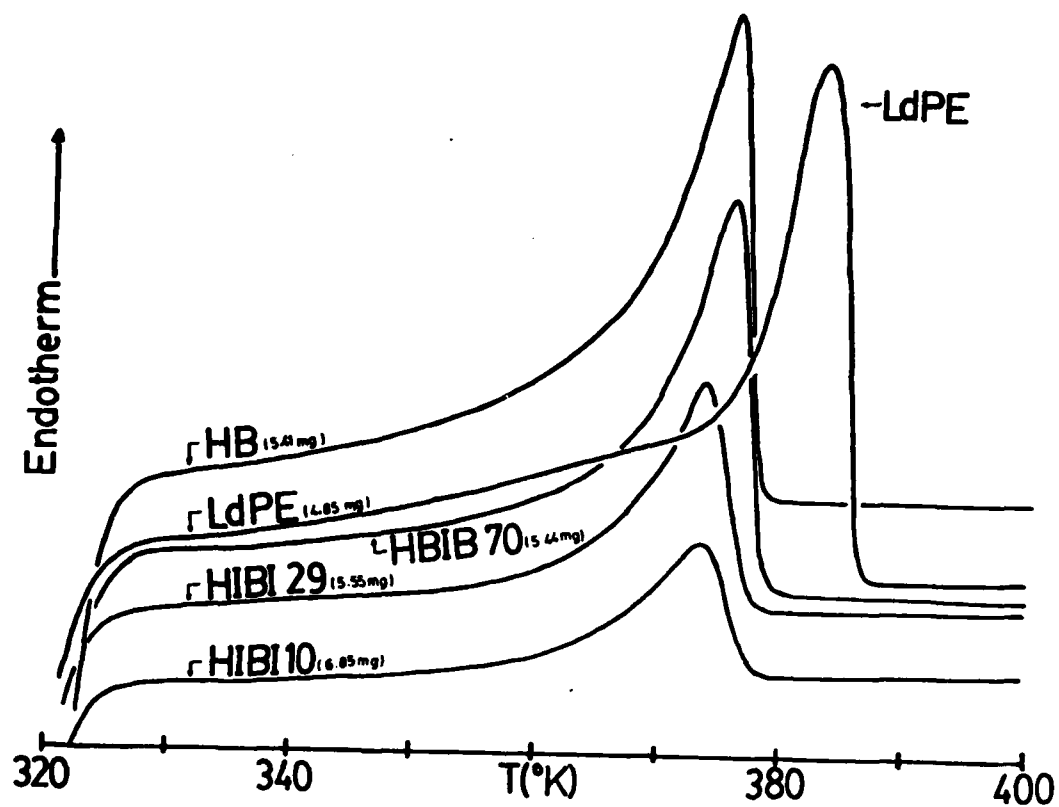


Fig. 2

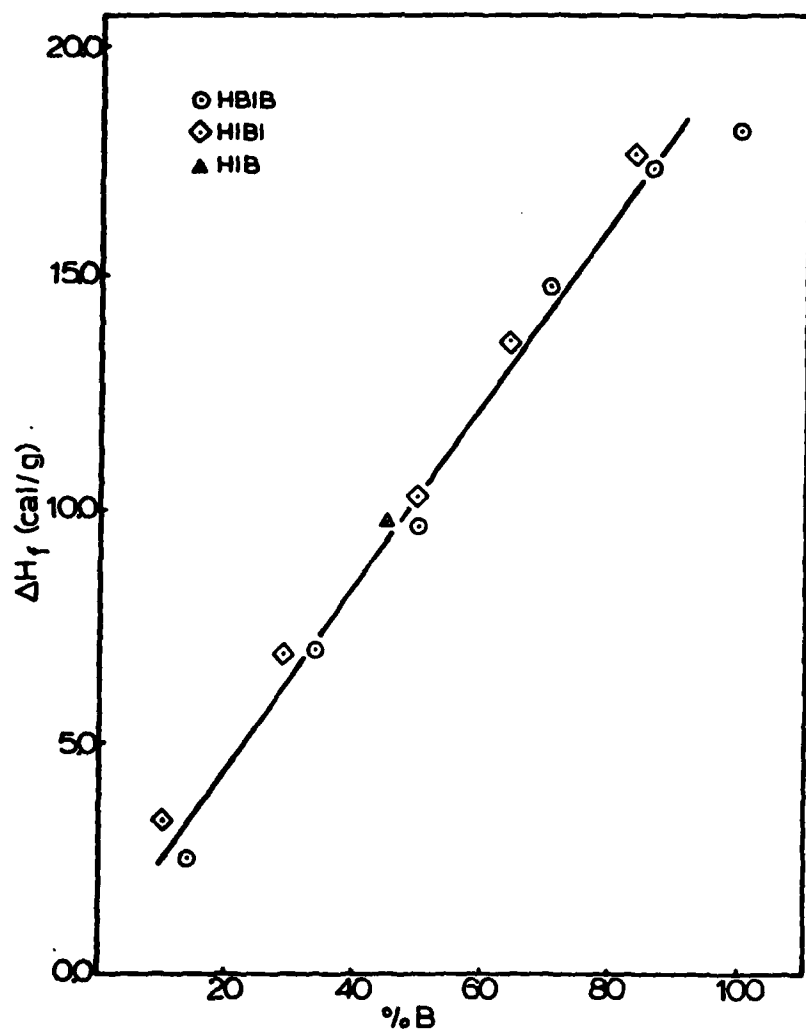


Fig. 3

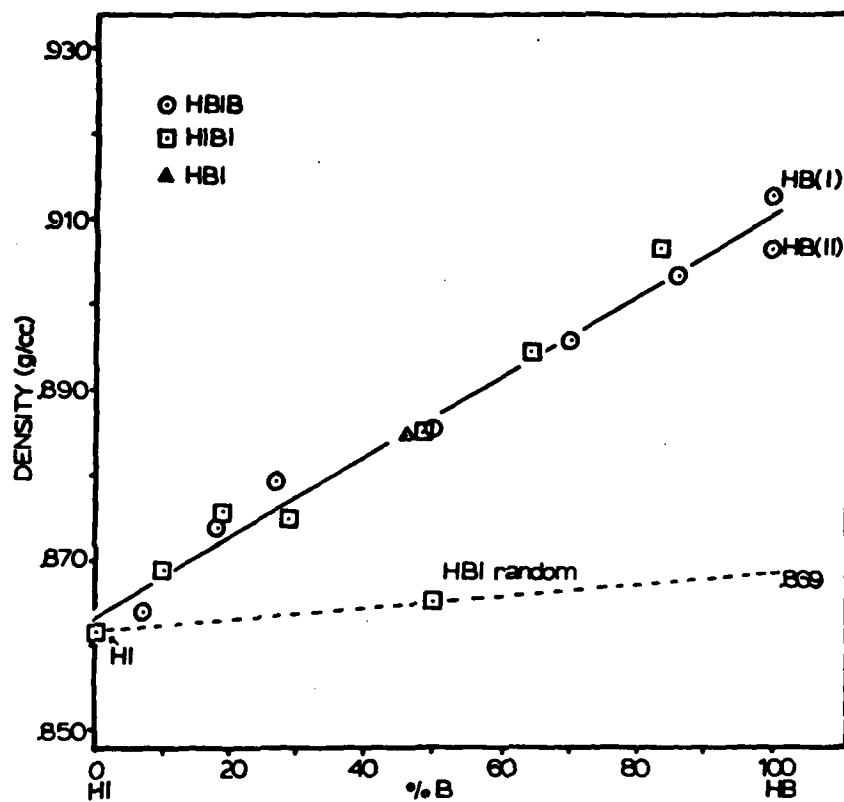


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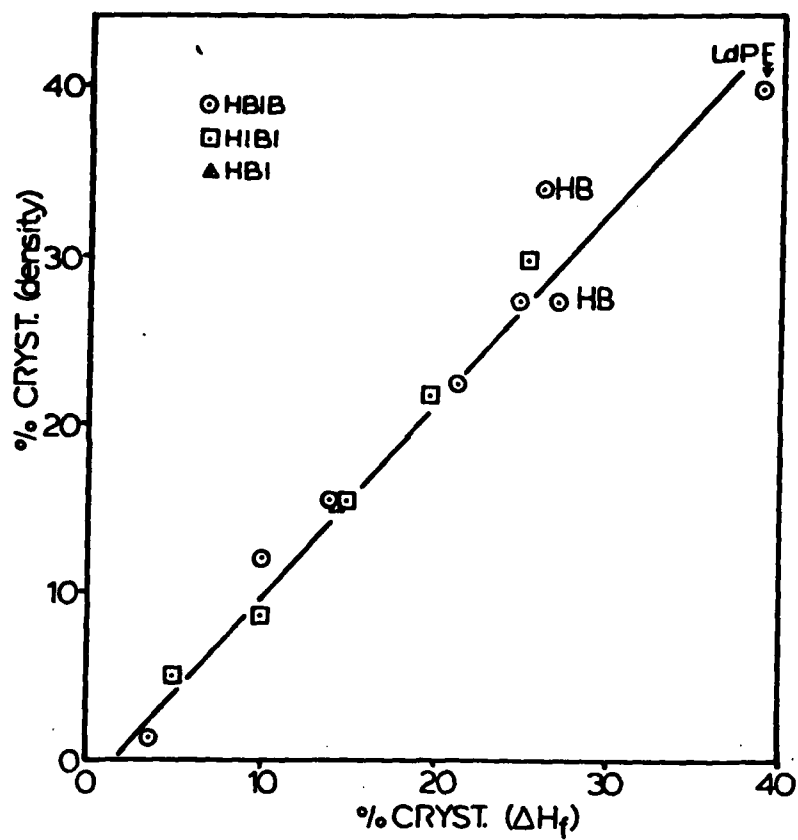
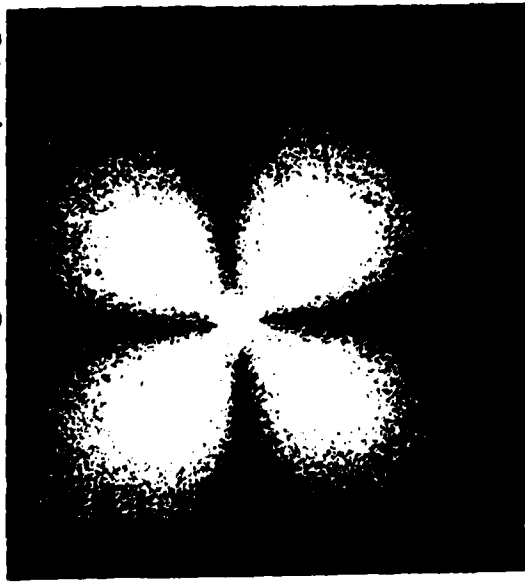
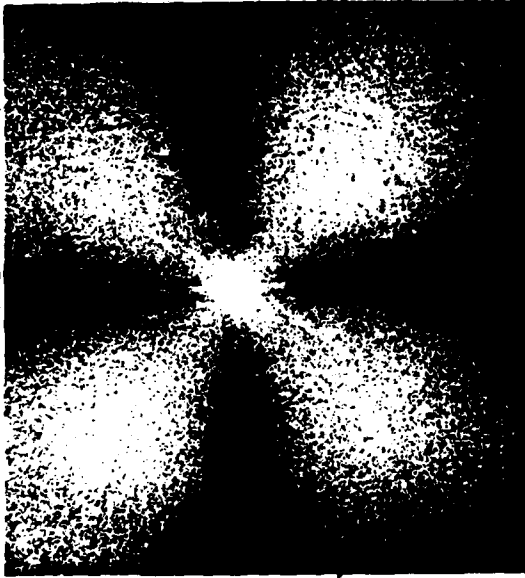


Fig. 5

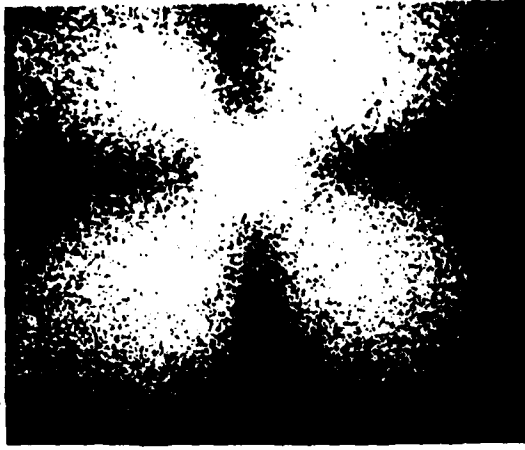
HB TOL 1/25



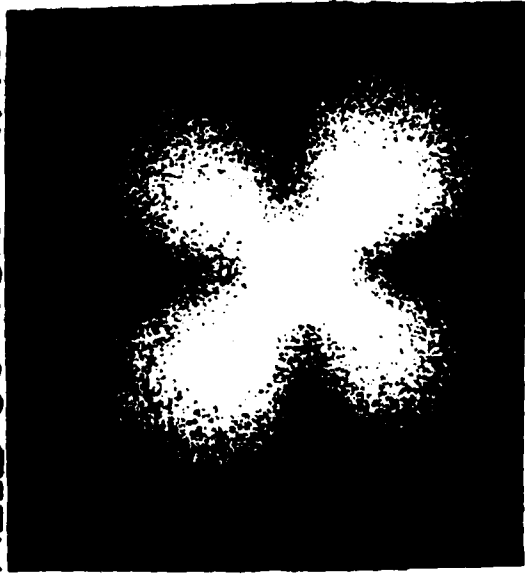
HBIB-86 TOL 1/25



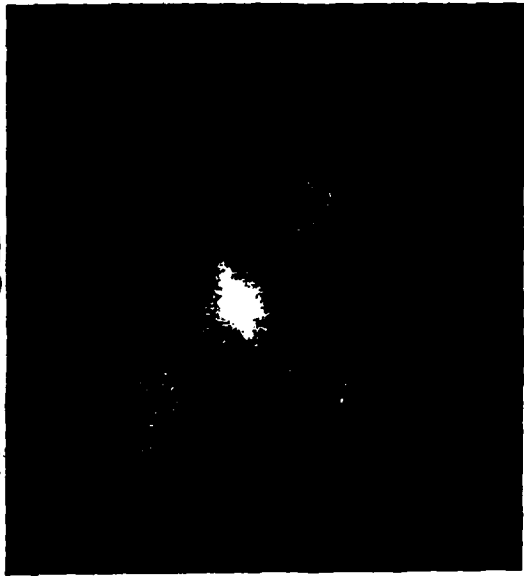
HBIB-70 TOL



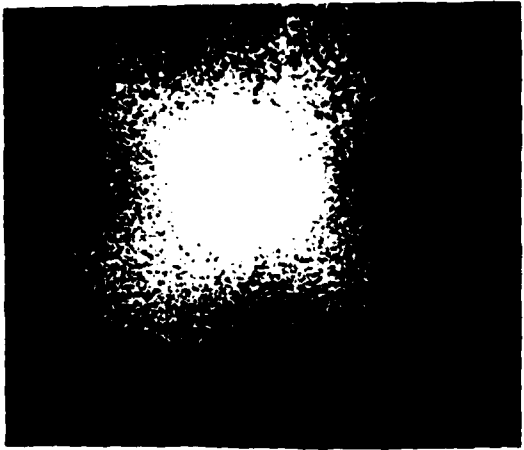
HBIB-50 TOL 1/10



HBIB-27 TOL 1/7

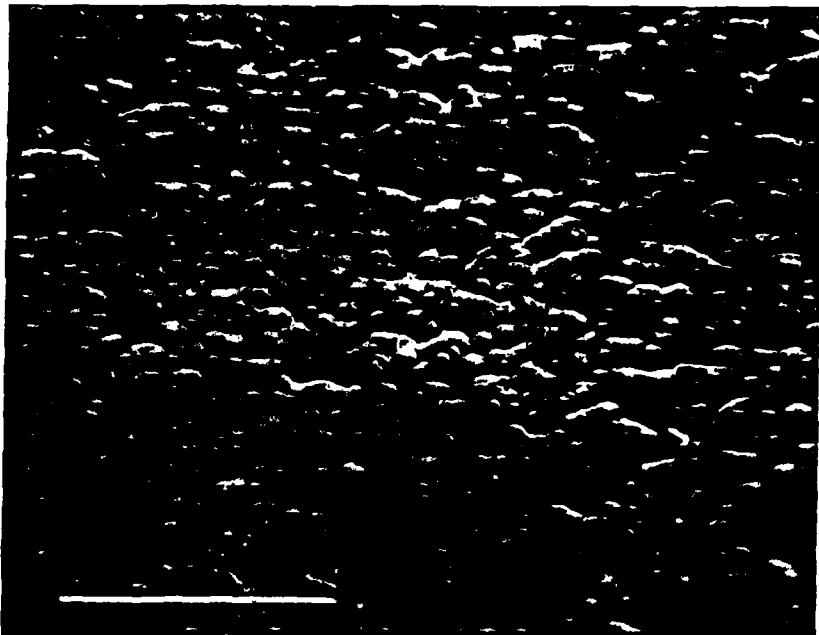


HBIB-7 TOL

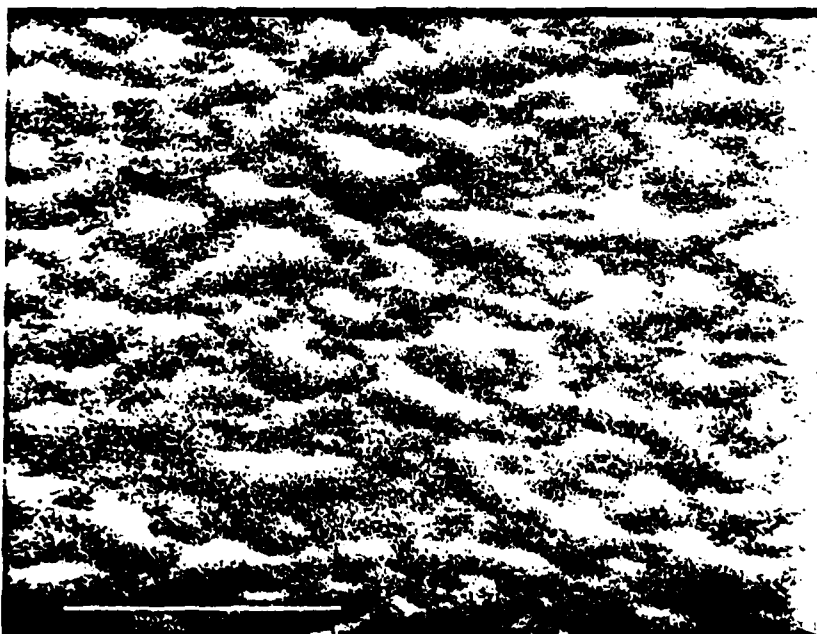


HB PQ 1/2





HB200 700X



HB1350-T02 700X

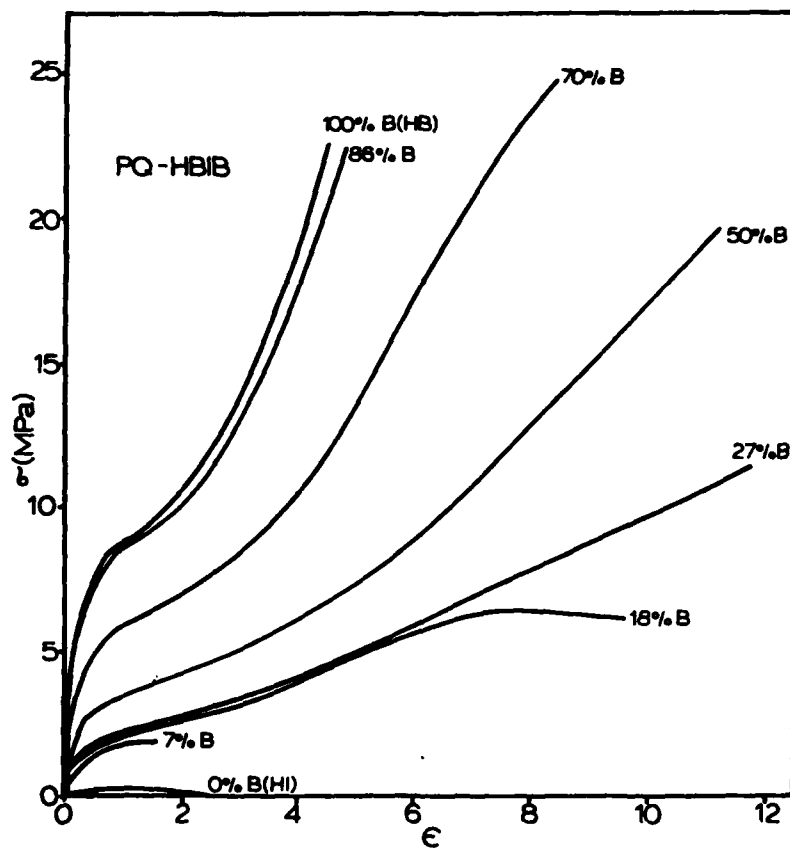


Fig. 8

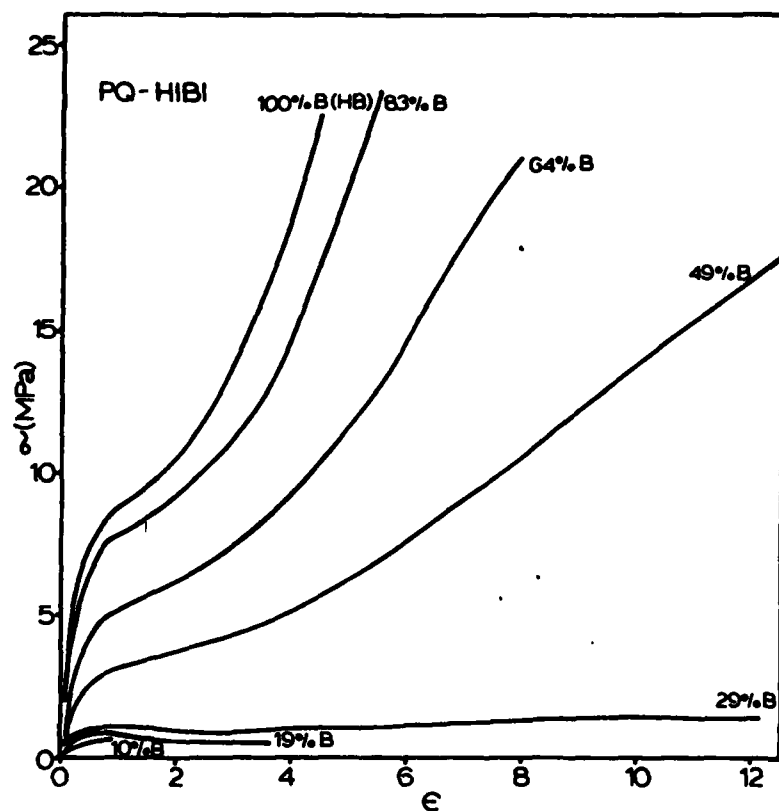


Fig. 9

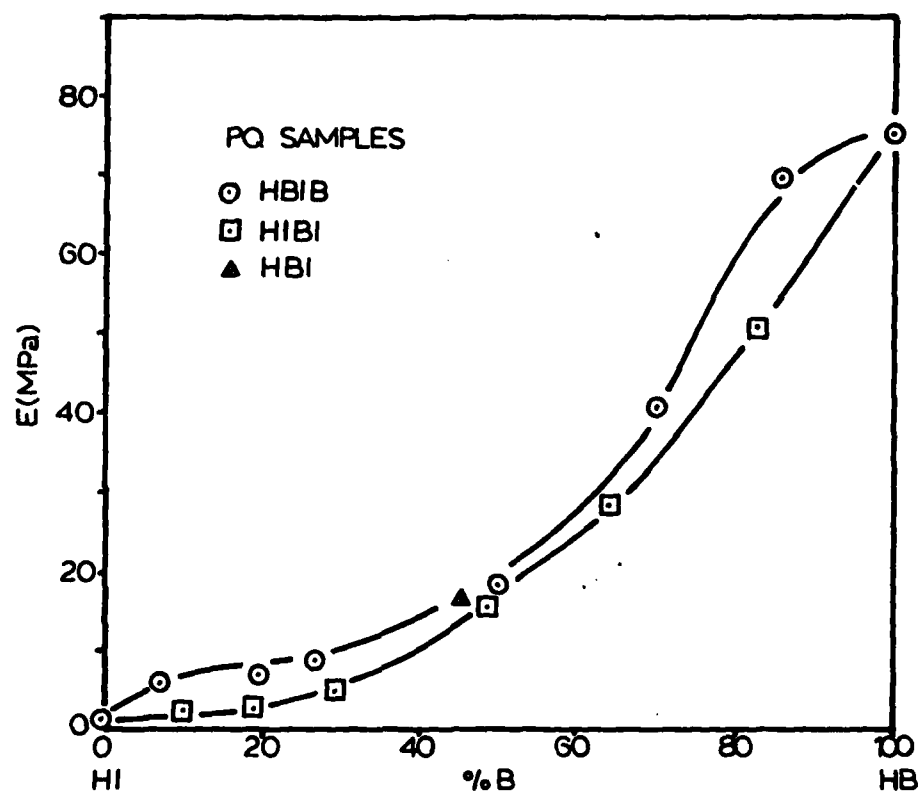


Fig 10A

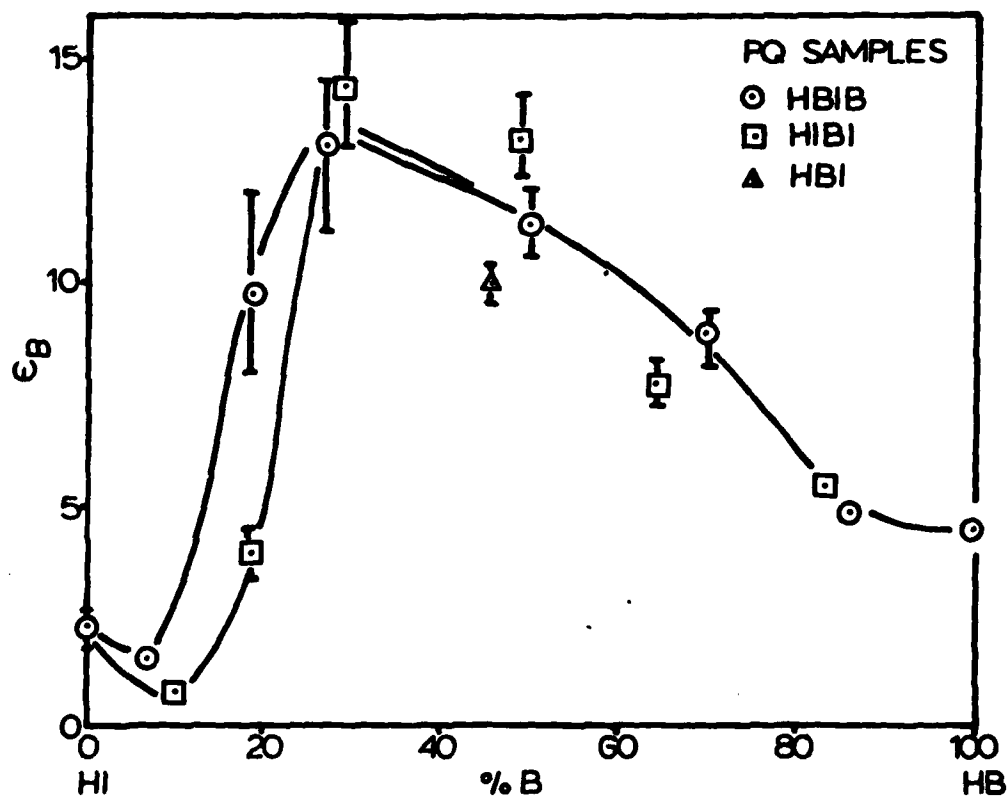


Fig. 10B

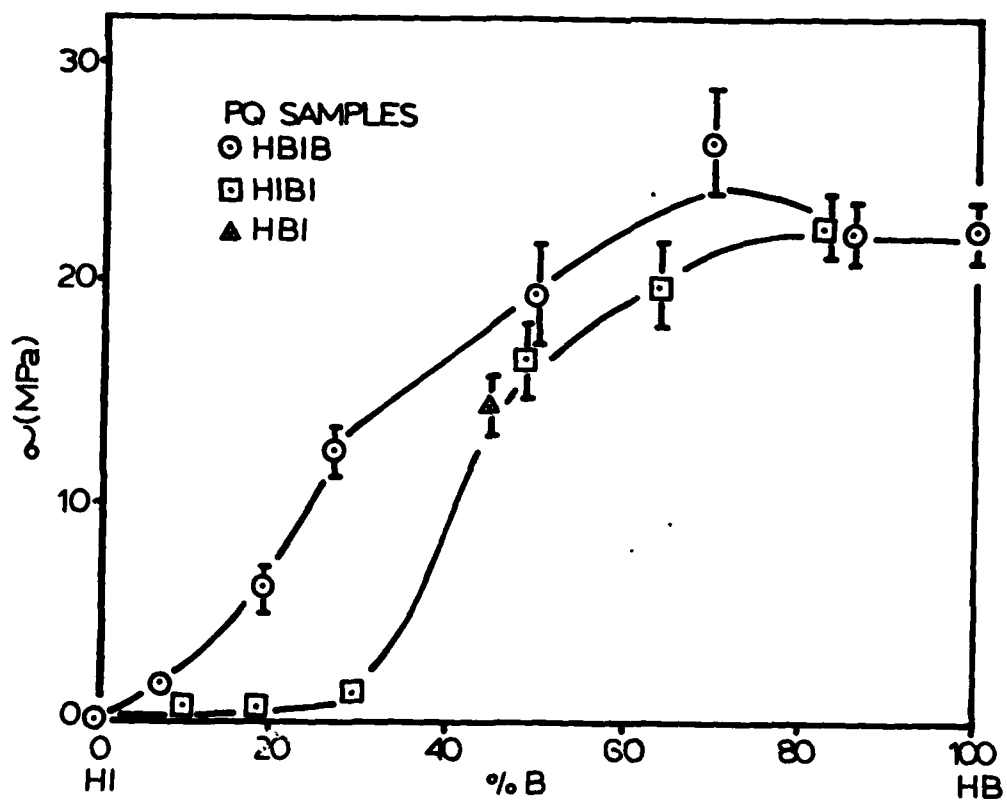


Fig 10C

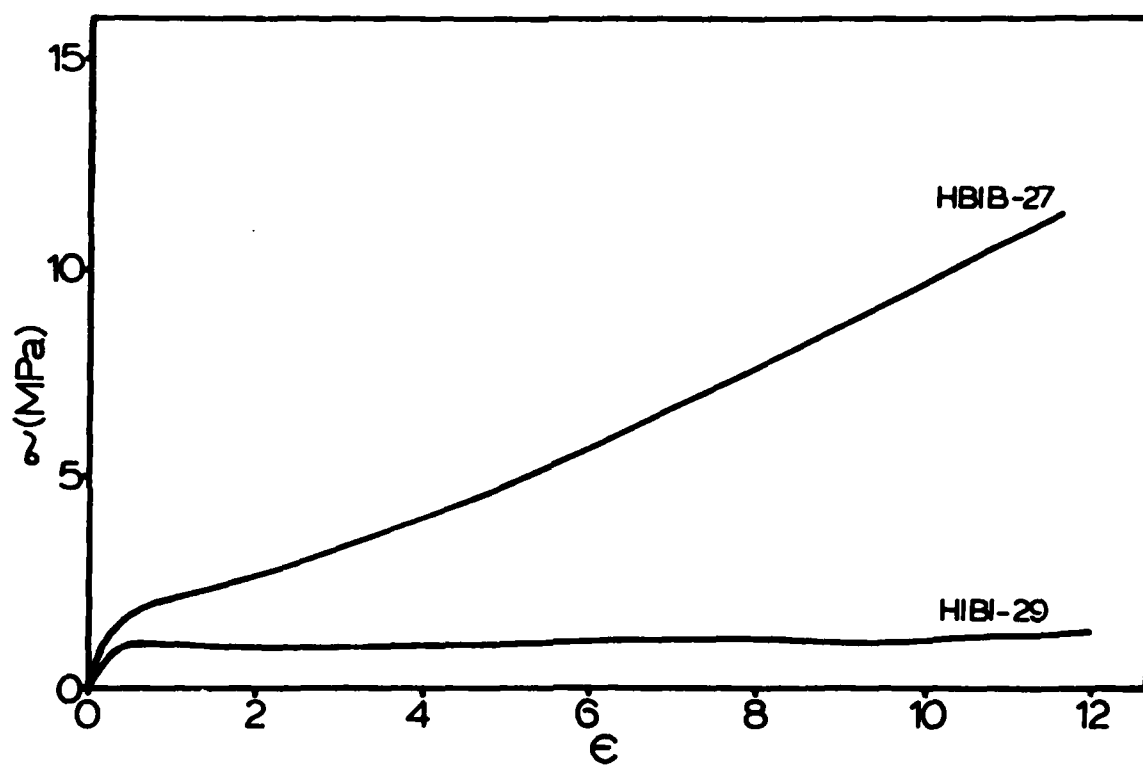


Fig. 11

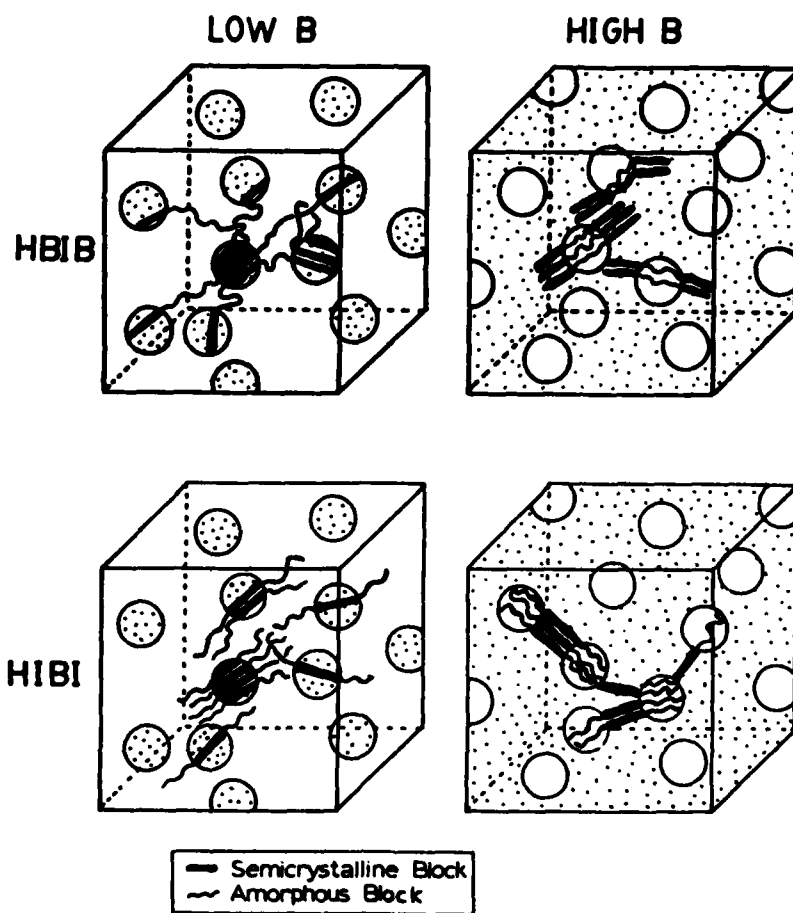


Fig. 12

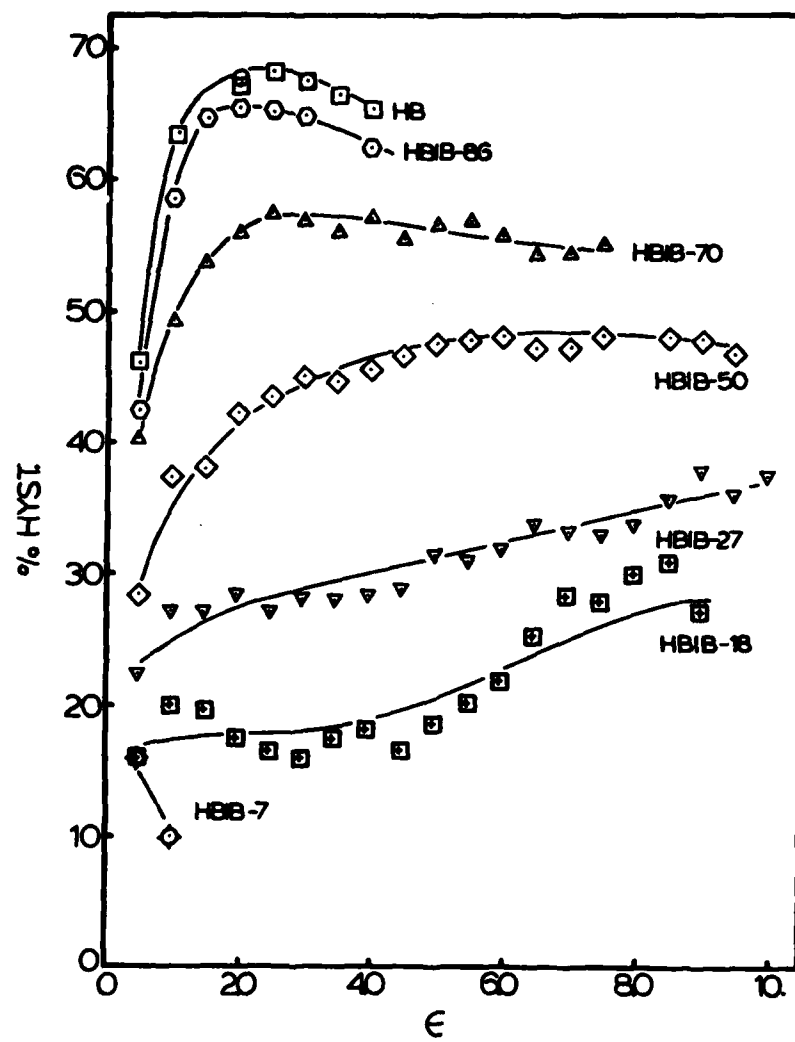


Fig 13A

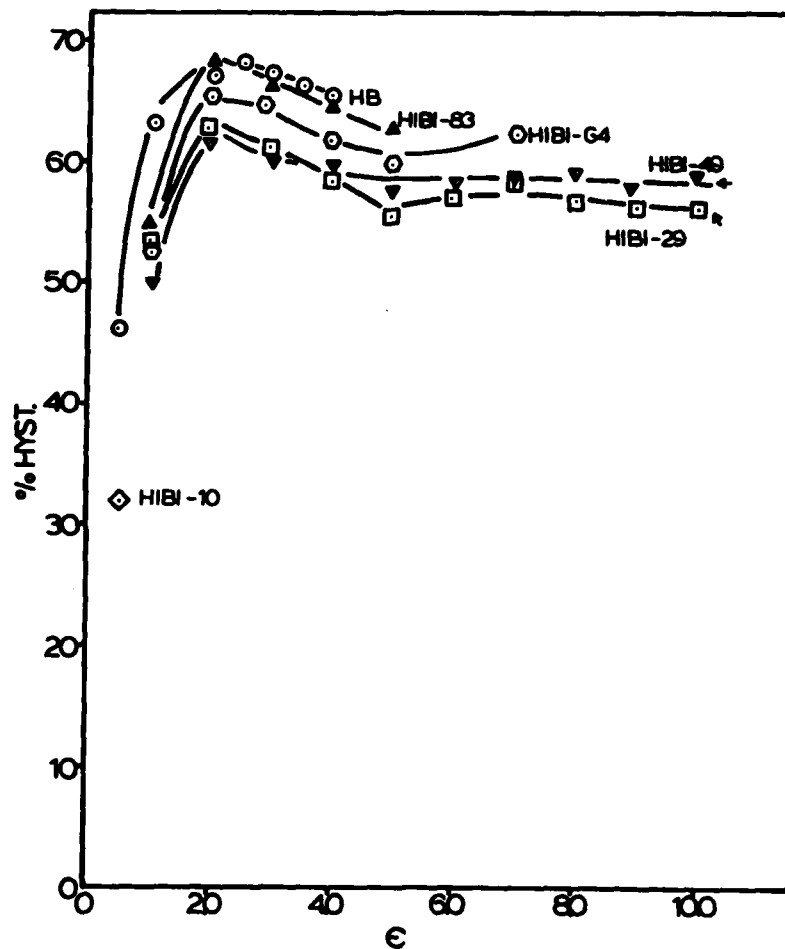


Fig 13 B

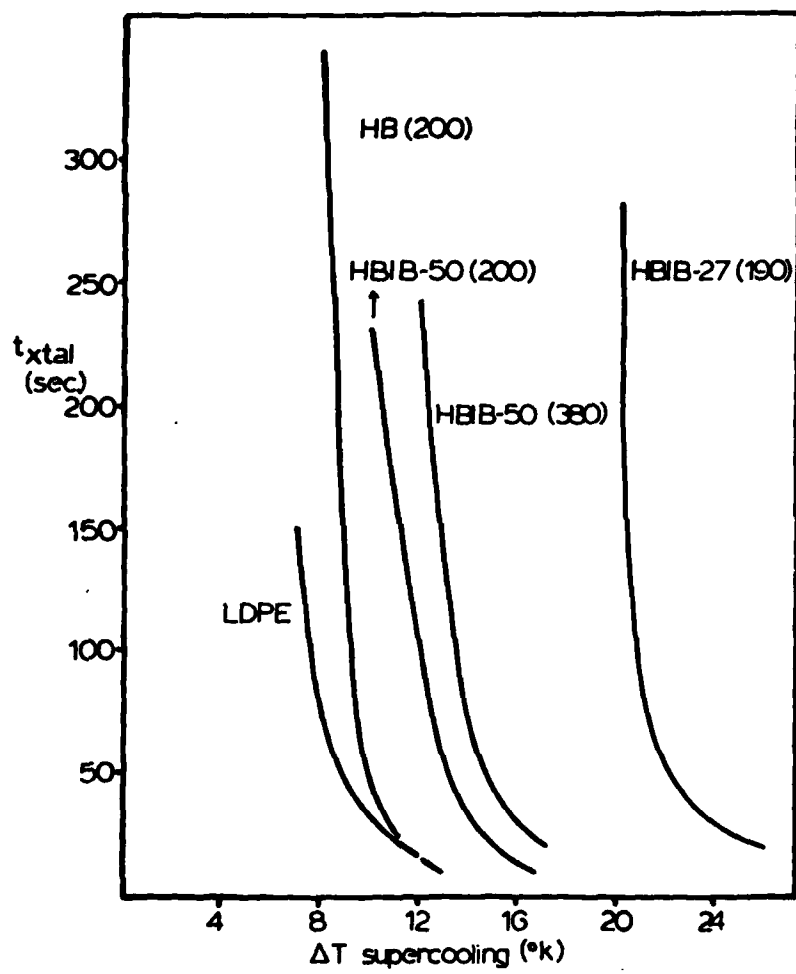


Fig 14 A

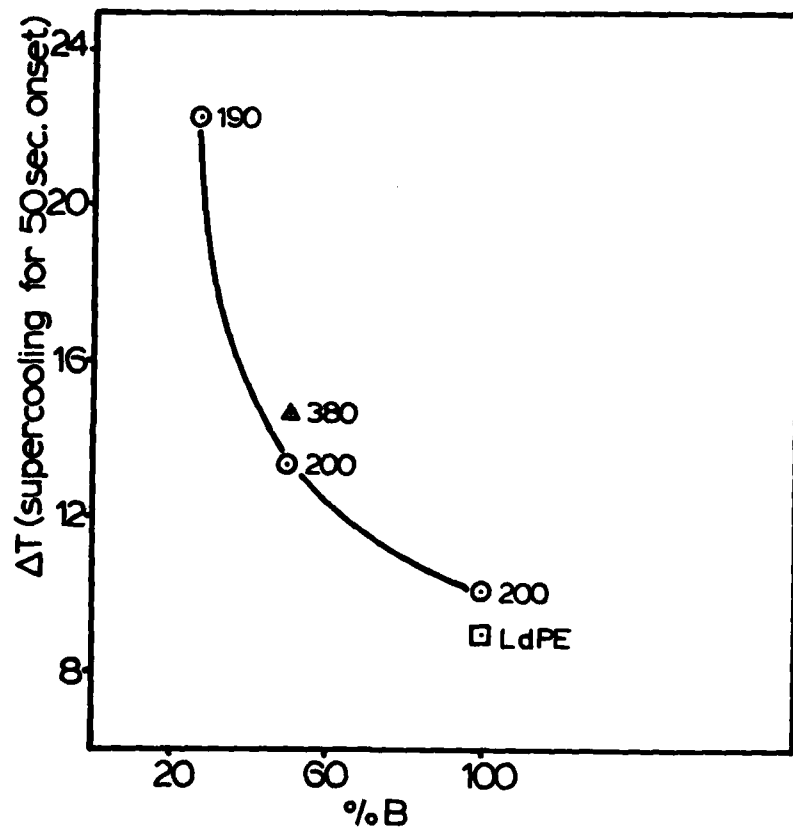


Fig 14B

IV. Chemorheology.

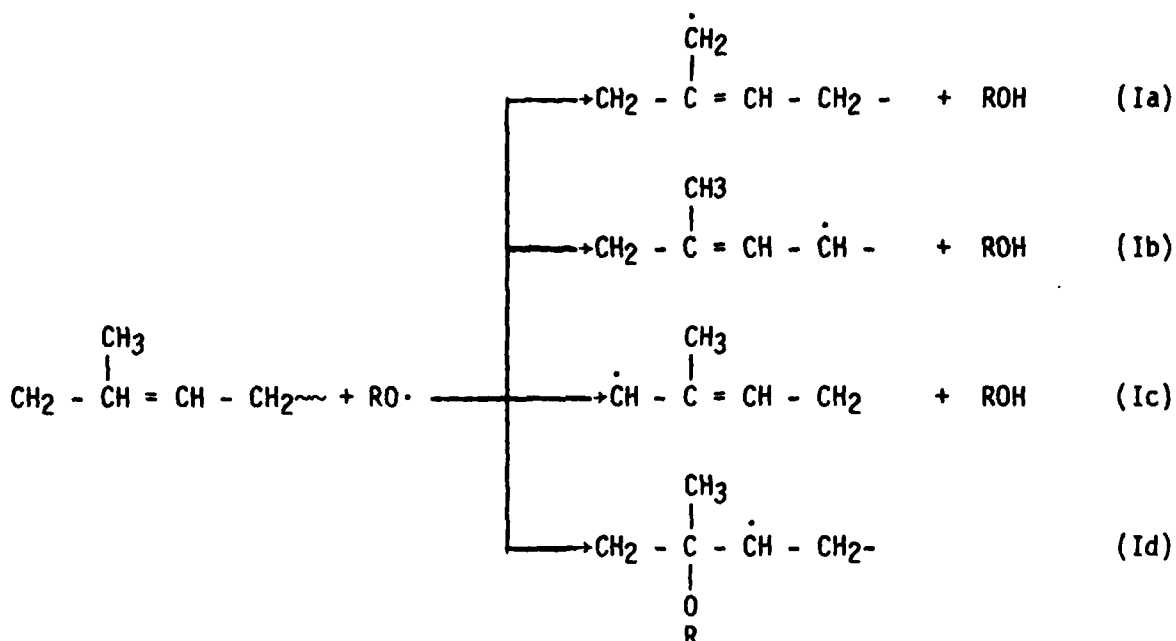
IV. CHEMORHEOLOGICAL STUDIES

INTRODUCTION

Little information exists that describes the structure property behavior of block copolymers where both components are in the rubbery state⁽¹⁾. Most research on block copolymers has been performed on materials where one component is glassy or crystalline at the use temperature and the other is rubbery at the same temperature. Typically, the objective is to produce a thermoplastic elastomer with a hard domain morphology that reinforces the soft matrix and simultaneously provides physical crosslinking. This is achieved by the synthesis of a block or segmented copolymer where the two components possess a sufficient difference in solubility parameters, and are of high enough molecular weight to promote microphase separation. An interesting situation regarding rubber-rubber block or random copolymers is defined by the case where the individual components display opposing chemo-rheological behavior. For example, suppose one of the blocks is prone to principally degradative chain scission while the other leads to extensive crosslinking. In this case, one might anticipate that with the proper choice of the components, composition ratio, and possibly suitable molecular architecture that these factors could all influence the chemo-rheological behavior of the system and yield materials with improved properties. Research published on the homopolymers^(2,3,4) has suggested to us that the butadiene-isoprene random copolymers may be such a system.

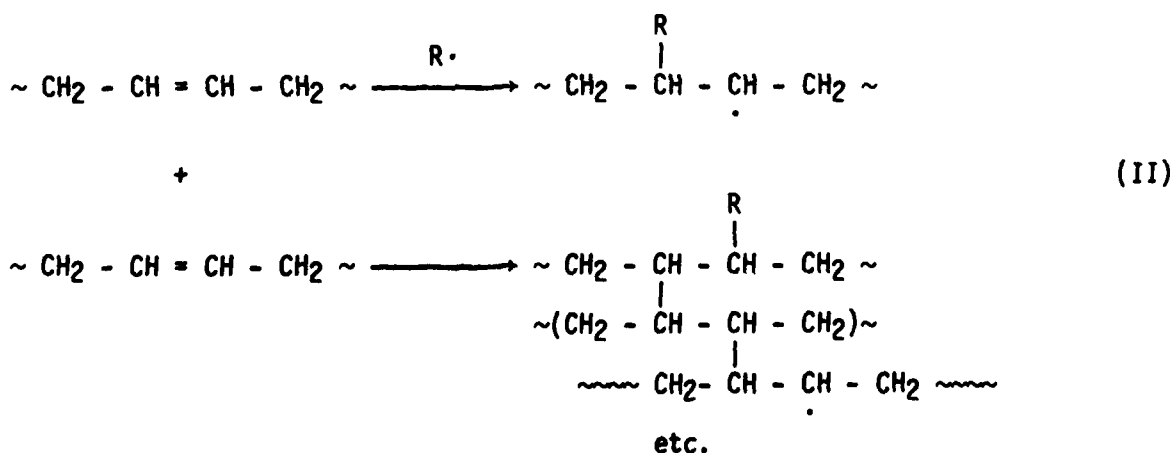
Tobolsky et al.⁽²⁾ have extensively studied the chemo-rheological behavior of poly(isoprene) and poly(butadiene) homopolymers vulcanized by various methods. Both natural and many of the synthetic rubbers are particularly susceptible to atmospheric oxidation because they contain reactive allylic C-H and olefinic $\begin{array}{c} | \\ -C=C- \end{array}$ groups. In this regard it has been

suggested that poly(isoprene) has four sites which are susceptible to attack by alkoxy radicals(5):



Abstraction of hydrogen predominates here over radical addition.

Poly(butadiene), on the other hand, displays quite different behavior. In addition to possible chain scission reactions, the absence of the methyl group affects the -C=C- group stability and the material becomes susceptible to extensive crosslinking at the vinyl group; possibly by a chain reaction "polymerization" step as outlined in equation II(6).



The 1,2 microstructure which is present at the level of ~6% or higher in poly(butadiene) (equation III) is particularly reactive.



Oxidative scission at temperatures above 100°C has commonly been studied by continuous and intermittent stress relaxation experiments^(2,7). The former includes normal stress relaxation at high temperatures where the material is deformed to a fixed elongation and the stress is followed as a function of time. This procedure provides information on chain scission effects and additional crosslinking due to chemical effects, e.g., peroxides or as shown in Scheme II above. Crosslinks formed by chains severed in the oxidation process are formed after relaxation of the initially stretched chains. Since the new crosslinks are formed from these undeformed chains, they do not contribute to the stress. By contrast, intermittent stress relaxation involves measuring the stress at a fixed elongation at relatively widely spaced time intervals. Intermittent measurements provide information on chain scission and/or additional crosslinking occurring in the network, including those crosslinks formed from active chains "cut" during the oxidation process (reversible chain scission). Methods that combine and simultaneously measure both continuous and intermittent effects have been proposed and utilized^(8,9). In general, both continuous and intermittent stress relaxation experiments together provide insight into the chemo-rheological properties of the polymer system under consideration, as has been well documented by Tobolsky et al.⁽²⁾ and Murakami⁽⁷⁾.

Tobolsky demonstrated that both radiation cured cis-1,4 and emulsion synthesized polybutadiene polymers displayed a stress increase during intermittent stress relaxation experiments⁽¹⁰⁾. Surprisingly, when dicumylperoxide (DCP) was used as a curing agent, the stress decayed steadily during intermittent measurements conducted in air. However, in vacuum the material displayed a rather high degree of crosslinking and the observed stress increased. Murakami et al. performed similar experiments using DCP cured cis-1,4 polybutadiene (PB-DCP) and cis 1,4-polyisoprene (PI-DCP). Their data showed that polybutadiene vulcanizates display a faster stress decay behavior than polyisoprene at the same temperature. Murakami⁽⁷⁾ speculated that there might be weak points near the crosslink sites in PB-DCP which are highly reactive to oxidative chain scission. DCP linking of rubbers involves hydrogen abstraction from the allylic C-H bond and the subsequent formation of polyisoprenyl or polybutadienyl radicals, which are stabilized by allylic resonance as discussed earlier⁽⁶⁾.

It has been observed⁽⁶⁾ that polybutadienyl radicals are more reactive than the polyisoprenyl counterpart and that direct addition to double bonds by this radical is an alternative route to that of recombination, for the formation of crosslinks (reaction II). Murakami⁽⁷⁾ suggested that the hydrogen atoms of the crosslink points in poly(butadiene) are selectively abstracted leading to chain scission near crosslink sites, thus accounting for his data. Our own view regarding Murakami's suggestions is that the behavior of poly(butadiene) is dominated by crosslinking reactions, although chain scission may still be significant. Radiation curing results in the same type of crosslinks as when peroxide is used. The fact that stress increases in intermittent stress relaxation experiments carried out on radiation cured poly(butadiene) supports the idea of extensive crosslinking occurring in this polymer.

Not all block copolymers display microphase separation. In the case of amorphous polymers, the extent to which phase separation occurs depend on the thermodynamic considerations, which include such features as the molecular weight of the blocks and the degree of block interaction⁽¹¹⁾. The differential solubility (Δ), defined as $(\delta_1 - \delta_2)$ allows a semi-quantitative assessment of the compatibility characteristics of the blocks. The isoprene-butadiene system offers a unique morphological behavior since the " Δ " value is very small (~ 0.3) and the copolymer might be expected to display a homogeneous morphology up to very high molecular weights. Indeed, Ramos and Cohen⁽¹²⁻¹⁵⁾ have reported that the isoprene-butadiene diblock copolymers with 250,000 for a total molecular weight display a homogeneous morphology. Their conclusion is based on the presence of a single T_g from dynamic mechanical and thermomechanical analysis and the successful fitting of the data to mechanical copolymers models. These models rely on temperature composition shifts which in turn depend on additivity of free volume in the individual homopolymers. McGrath et al.⁽¹⁶⁾ confirmed and expanded this view since thermal experiments (DSC) showed that diblock samples with molecular weights up to 400,000 were still one phase in agreement with the theory of Meier⁽¹¹⁾ and others.

Ramos et al. showed that polymer blends of poly(butadiene) and poly(isoprene) are incompatible and display a two-phase morphology. It should be emphasized in addition, that it is difficult to characterize possible phase separation in the isoprene-butadiene system by direct techniques such as small angle X-ray scattering due to the small difference in electron densities of the components and hence, little scattering is detected. We believe that our data reported here lends additional support to the conclusions made by Ramos and Cohen, and McGrath and coworkers regarding morphological homogeneity.

Experimental

The polymers used in this study were synthesized by anionic polymerization using sec-butyllithium initiators in hexane solvent⁽¹⁹⁾. Both polydienes contained over 90% of the 1,4 microstructure as revealed by IR spectroscopy (Table I). Dicumyl peroxide (recrystallized) was added to the purified polymers in a 5% polymer solution in hexane. The recovered dry cast films were then compression-molded at 150°C to induce the peroxide crosslinking reaction. For a fixed peroxide content and fixed crosslink density, it was necessary to cure the films for different times, since the efficiency of the crosslinking reaction is composition dependent. Specifically, the samples with high isoprene content required longer curing times than those samples with high poly(butadiene) fractions. The crosslink density was checked by swelling experiments⁽¹⁷⁾ and by utilizing rubber elasticity theory in conjunction with equilibrium stress measurements from stress-relaxation tests carried out at ambient temperature⁽¹⁷⁾. The cured films were extracted in a soxhlet for 24 hours in hexane to remove the sol fraction (~1%), and for another 24 hours in acetone to extract any remaining peroxide or stabilizer decomposition products.

The stress relaxation experiments were carried out using a UTM-II tensilon in conjunction with an oven and a TC4 proportional temperature controller. All tests were performed in air at 100°C with a elongation rate of 50 mm/min and a constant elongation of 50%. The dog-bone specimens were 20 x 5 mm and thickness was .25 mm so that diffusion effects were minimized⁽¹⁸⁾. It took about 30 seconds for a complete cycle of deformation-recovery to be performed. This time was considered satisfactory in light of the time span of the intermittent experiments.

Discussion

Table I summarizes the properties and the characteristics of the homopolymers and copolymers studied. All materials had possessed a value of \bar{M}_n near 200,000 and were nearly monodisperse as revealed by gel permeation chromatography (GPC). The polymers also contained more than 90% of the 1,4 microstructures except the polybutadiene homopolymer which contained 25% of the 1,2 isomer. Figure 1 shows the effect of peroxide initiated crosslinking. It is of interest to note that to achieve a swelling index of 2.5 at 2%, by weight of peroxide, curing for only 90 seconds was required for the poly(butadiene). On the other hand, 2% by weight and 2 hours of curing were necessary for the poly(isoprene) to obtain the same degree of crosslinking (as judged by swelling). The high reactivity displayed by the poly(butadiene) sample cannot be attributed solely to the 1,2 structure alone since vulcanization showed a non-linear dependence on composition. For example, the sample with 73% poly(isoprene) (BIB-27) required only 20 minutes of curing with 2% peroxide to achieve the same swelling index. A plausible explanation for this behavior is that the efficiency (i.e., kinetic chain length) or the kinetics of the crosslinking reaction depicted in reaction II is very high. Although the mixed morphology of the system might be playing an important role in this behavior, no conclusive evidence is available on that point to actually correlate the morphological texture of the polymer with its curing behavior.

Additional information was gained by examining the continuous stress-relaxation data shown in Figure 2. Specifically, there is a systematic increase in the stress decay as a function of increasing poly(isoprene) content. On the other hand, increasing the poly(butadiene) fraction clearly increases the rate of crosslinking and therefore decreases the stress-decay process.

The intermittent experiments offer additional evidence to the conclusions made in the discussion above. In particular, the stress displayed by the poly(butadiene) homopolymer increases with time and almost doubles in value after two hours. In fact, the samples showed a high degree of crosslinking and broke upon extension. The intermittent measurements also show a systematic decrease in the stress growth as the composition changes from pure poly(butadiene) to pure poly(isoprene). The sample with 27% poly(butadiene) for example displays an interesting behavior where the stress still shows a dramatic increase with time indicating that the efficiency of the oxidative crosslinking is still rather higher than that of the chain scission process. It should be pointed out, however, that this behavior is in contrast to earlier conclusions made by Murakami⁽⁷⁾ regarding the stress-relaxation behavior of cis 1,4 poly(isoprene) and cis 1,4 poly(butadiene) homopolymers. However, our results are very consistent with the observations of many rubber technology studies that show PB systems to harden⁽³⁾ and PI systems to become tacky. We feel that the behavior of our polymers and copolymers can be accounted for by three main mechanisms: (1) irreversible chain scission of poly(isoprene); (2) reversible chain scission of polybutadiene; and/or (3) crosslinking or polymerization of poly(butadiene). The first of these factors is evident since little difference occurs between the intermittent and continuous stress-relaxation behavior of polyisoprene. However, while reversible chain scission has little contribution to the stress behavior in the continuous experiments since any chains severed and reformed will do so in the relaxed state, the intermittent measurements reveal that this phenomena might be rather extensive in poly(butadiene) and accounts for the high stress displayed by the polymers containing poly(butadiene). However, the stress increase could also be attributed to the crosslinking or the polymerization

reaction of poly(butadiene) (Reaction III) since polybutadiene homopolymer and copolymers of poly(butadiene) display a decreased stress decay behavior compared to that of pure poly(isoprene). We speculate that the stress increase in these polymer is due to this phenomena and not necessarily due to reversible chain scission.

Figures 2 and 3 also reveal that the 50/50 composition of the random, diblock, and triblock copolymers (Random-50, BI-50, BIB-50, IBI-50) display a rather interesting behavior. The stress decay is found to be independent of the molecular architecture. This observation, along with the systematic decrease in stress-decay with increasing polyisoprene content and the crosslinking data in Figure 1 suggest a rather homogeneous (well-mixed) morphology in accordance with earlier observations(12-16). That is, one would have likely anticipated a different behavior than that displayed in Figures 2 and 3 if the material was phase separated since the crosslinking and oxidative scission process would have involved selective discrete regions that would be strongly dependent on the morphological texture of the polymer.

Conclusions

This work emphasizes the novel chemorheological behavior of isoprene-butadiene copolymers. At relatively high temperatures, there are two competing processes that affect the mechanical property of the copolymers. The first may involve both reversible chain scission and rapid crosslinking while the other is irreversible chain scission. The first of these most important degradative reactions is dominant in poly(butadiene) while the second seems to be in poly(isoprene). However, in the block copolymers studied, the behavior of the samples was dependent on the composition but was independent of the molecular architecture. The systematic behavior displayed by the polymers suggest well-mixed morphology as has been reported by others, using more conventional methods for miscibility assessment.

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Table I

Characteristics of Polybutadiene and Polyisoprene Homo- and Copolymer Materials

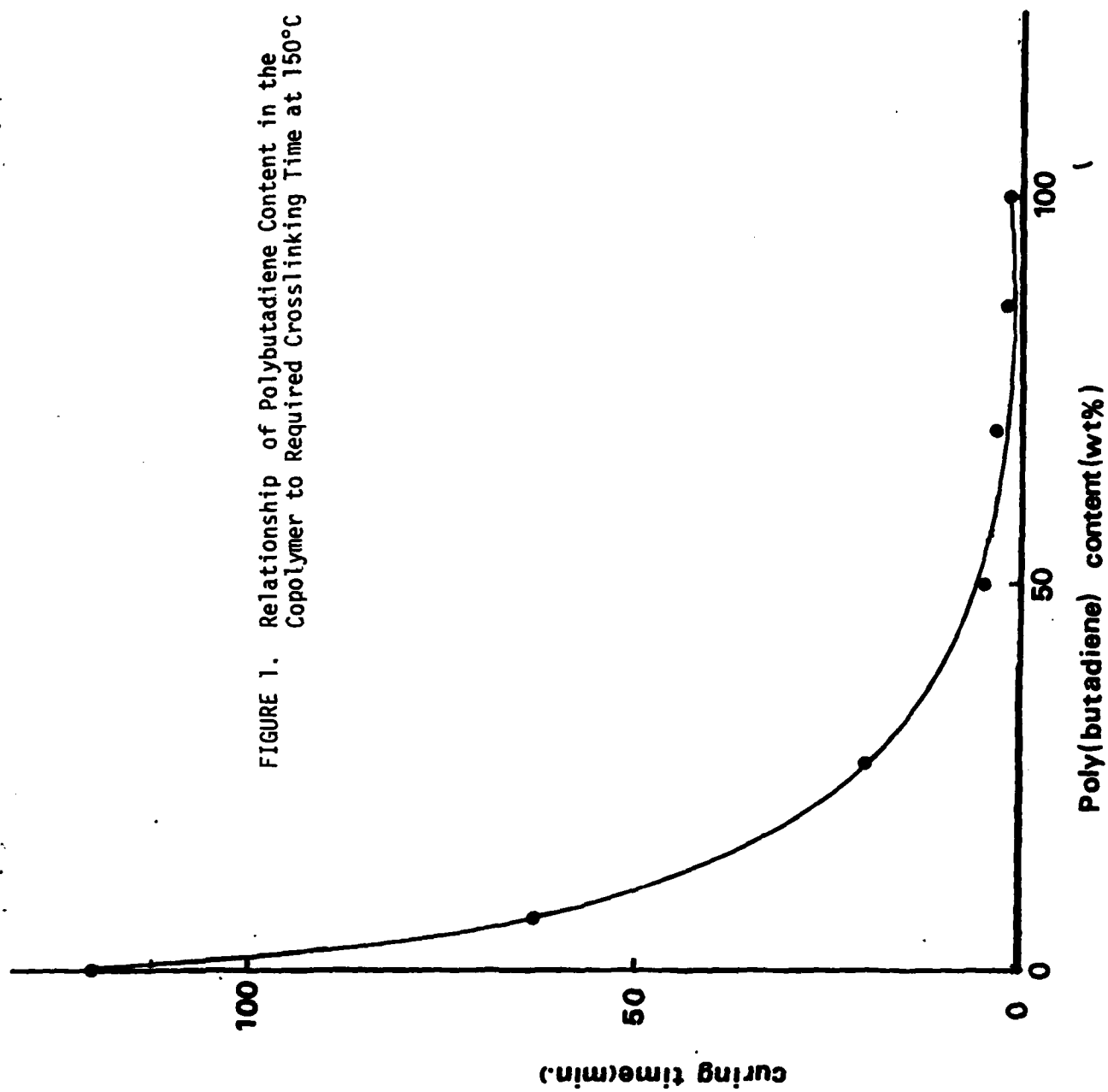
SYSTEM		$\langle M_n \rangle \cdot 10^{-3}$	CURING TIME (MIN)	(a)	SWELLING INDEX wt. swollen rubber wt. dry rubber	(b) M_c (from stress- relaxation)	POLYBUTADIENE ISOMERS ^(c) (%)
BI (Random)	50/50	190	5		2.6	5200	cis 1,4 trans 1,4 1,2
BI (Diblock)	50/50	195	5		2.65	5200	
BIB (Triblock)	27.5/45/27.5	225	5		2.65	5200	
BIB-50 (Triblock)	25/250/25	211	5		2.71	5400	
BIB-86	43/17/43	190	2.3		2.69	5300	
BIB-70	35/30/35	202	3.5		2.57	5200	
BIB-27	13.5/73/13.5	180	20		2.50	5150	
BIB-7	3.5/93/3.5	216	63		2.70	5400	
PI (Homopolymer)	---	200	120		2.60	5200	
PB (Homopolymer)	---	195	1.5		2.67	5200	

(a) 2% by weight dicumyl peroxide, cured at 150°C

(b) Stress relaxation at ambient and 50% elongation

(c) IR Data, not normalized, when this is done, typical values are 40, 53, and 7% for cis, trans, 1,2, respectively

FIGURE 1. Relationship of Polybutadiene Content in the Copolymer to Required Crosslinking Time at 150°C



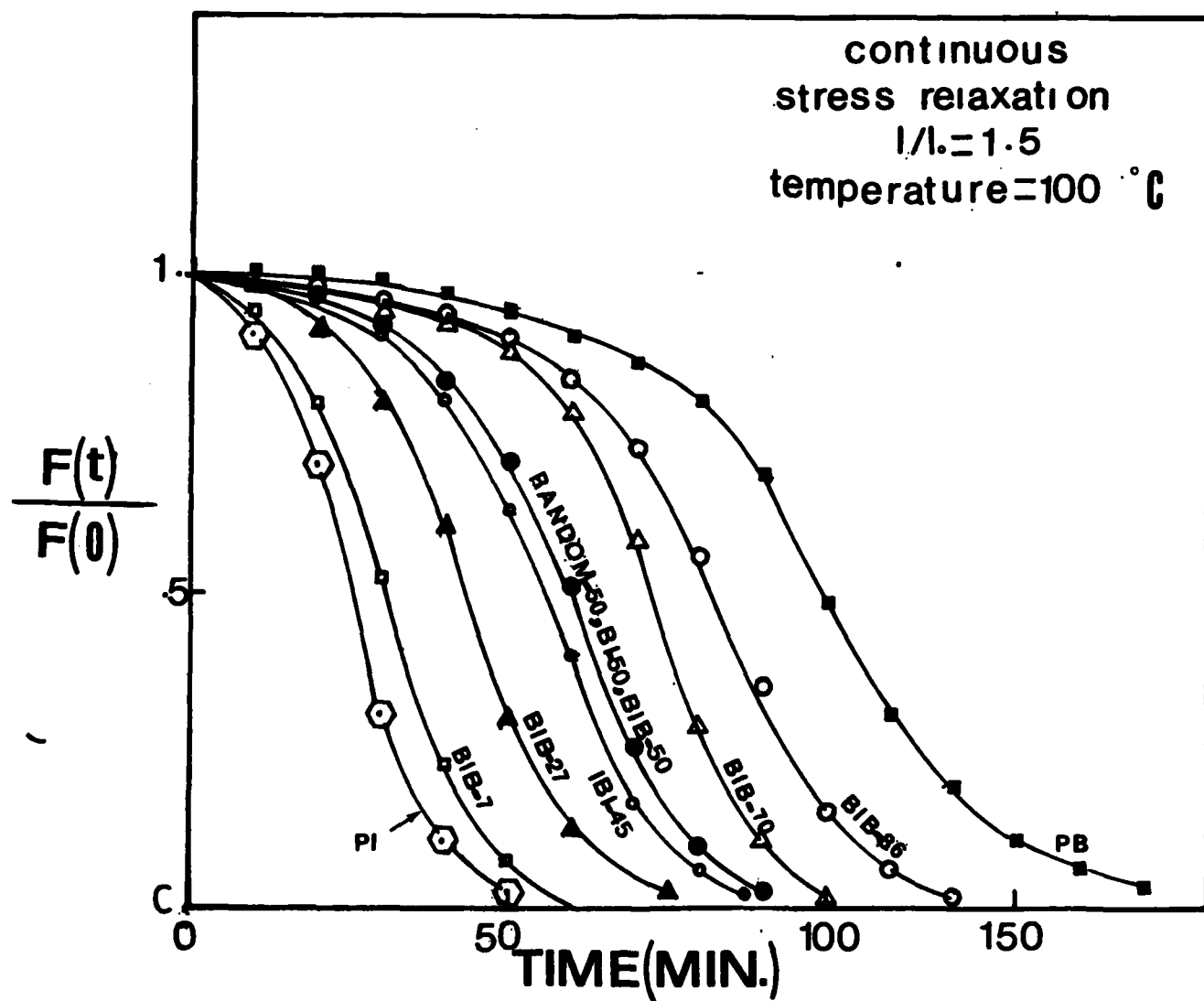


FIGURE 2. Effect of Copolymer Structure and Architecture on the Continuous Stress-Relaxation of Poly(Butadiene)-Poly(Isoprene) Peroxide Cured Networks

x

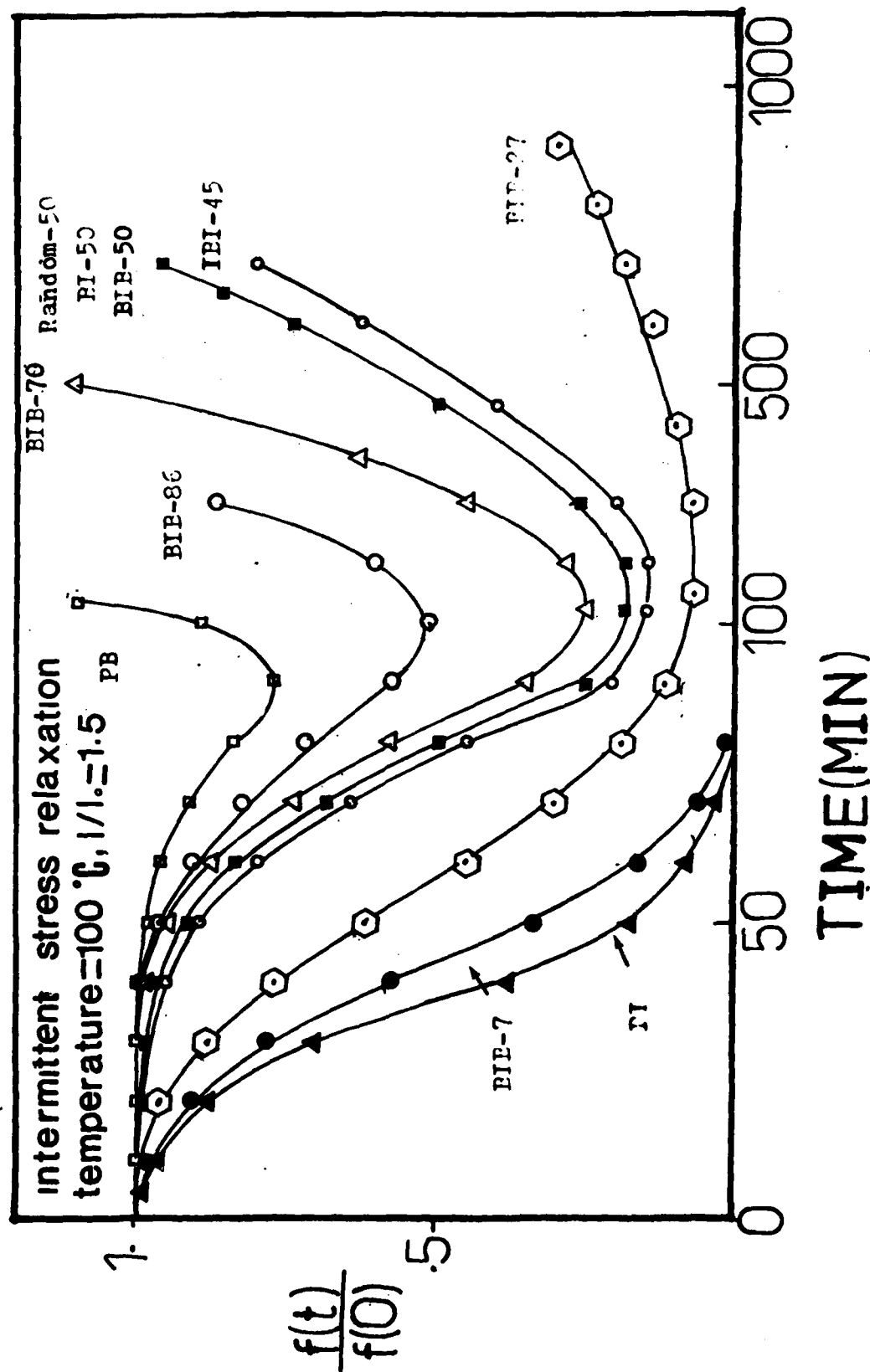


FIGURE 3. Effect of Copolymer Structure and Architecture on the Intermittent Stress-Relaxation of Poly(Butadiene)-Poly(Isoprene) Peroxide Cured Networks

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